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THE CHEMISTRY OF DISINFECTANTS IN WATER:
REACTIONS AND PRODUCTS

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Office of Drinking Water
Criteria and Standards Division

by the
Subcommittee on Disinfectants and Products
of the
Safe Drinking Water Committee

Board on Toxicology and Environmental Health Hazards
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The report begins with a preliminary discussion of the character of the natural organic substances from which by-products of organic disinfectants are thought to originate. Subsequent sections describe the chemistry of chlorine, chloramines, halogens (bromine and iodine), chlorine dioxide, and, finally, ozone. The report contains a significant bibliography.

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THE CHEMISTRY OF DISINFECTANTS IN WATER: REACTIONS AND PRODUCTS

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THE CHEMISTRY OF DISINFECTANTS IN WATER: REACTIONS AND PRODUCTS

A major objective of this review of disinfectant chemistry is the identification of likely by-products that might be formed through the use of specific disinfectants. The review is part of a comprehensive study of the possible health effects of contaminants in drinking water. The prediction of possible products, which is attempted herein, is intended to be a guide to those contaminants that might require removal or toxicological evaluation; however, neither of these two aspects of the overall study is discussed in this report.

While there is some current research on using combinations of disinfectants sequentially, the chemical consequences and benefits of this strategy are not yet clear. This subject has been omitted from the report. Similarly the subcommittee did not review the chemical side-benefits of disinfection, such as removal of cyanides, phenols, and, possibly, many other compounds, although these side-benefits may be of considerable importance.

Although there is now a rapidly growing body of scientific literature on chlorine by-products in drinking waters, comparable information for other disinfectants is very scarce. The subcommittee felt that reviewing chlorine by-products in detail, while saying little about other disinfectants, could suggest (probably erroneously) that these alternate disinfectants are free of the difficulties that are encountered with chlorine. In an attempt to circumvent this problem, the subcommittee found it necessary to broaden its information base by reviewing not only data on potable water, but also studies on nonpotable water, such as treated sewage effluents, and on synthetic model solutions, the data from which might be applicable to potable waters. These studies on nonpotable water shed light on the chemistry of disinfectants in drinking waters, although it is obvious that many compounds that are produced in treated sewage or in artificial laboratory experiments may never be found in drinking waters. To avoid confusion, a clear distinction has been drawn throughout the report between information acquired from actual drinking waters and information derived from other sources.

A great deal of research on the chemistry of disinfectants is now in progress. An attempt was made to ensure that this report was current by contacting many scientists who are working in this field in the United States and abroad. However, in an active field such as this, any review can become rapidly outdated.

The report begins with a preliminary discussion of the character of the natural organic substances from which by-products of organic disinfectants are thought to originate. Subsequent sections describe the chemistry of chlorine, chloramines, halogens (Br_2 and I_2), chlorine dioxide, and, finally, ozone.

PRECURSOR COMPOUNDS AND THE HALOFORM REACTION

Since 1975, many investigators have assumed that the ubiquitous appearance of chloroform ($CHCl_3$) and other THM's (trihalomethanes, or haloforms) in chlorinated water can be explained by the mechanisms involved in the "haloform reaction" and that the principal precursors of THM's that are found in natural waters are humic substances. As discussed in the section pertaining to chlorine chemistry, the haloform reaction will proceed only if specific functional groups are present in the available pool of organic compounds. It is likely that the haloform reaction does occur when natural waters are chlorinated and that humic substances provide the necessary functional groups, but it is not certain that either of these postulates is true. For that reason, both topics--the haloform reaction and humic substances--merit further discussion.

The Haloform Reaction

The terms "trihalomethanes" and "haloforms" are synonymous, but the term "haloform reaction" is often misused in discussions of THM formation in natural waters. In recent literature, it has been used to mean any reaction between aqueous solutions of organic compounds and hypohalous acids that results in THM formation, but it actually has a classic chemical definition that is more restrictive. In the future, the expanded meaning may be preferred, but at present the term "haloform reaction" is inappropriate from a strict chemical interpretation, unless one is sure that the THM's are formed by reactions between hypohalous acids and compounds containing acetyl groups or substituents that can be converted to acetyl groups.

The classic haloform reaction, which is actually a series of well-defined reactions, has been known since the 1800's (Fuson and Bull, 1934). The earliest studies were conducted with nonaqueous solvents, high concentrations of organic compounds, and chlorine gas, but research since 1974 has focused more on defining the reactions that yield THM's under conditions that are closer to those more commonly encountered during the treatment of drinking water supplies.

Compounds, or classes of compounds, with the general formula CH_3CHOHR or CH_3COR (which includes ethanol, acetaldehyde, methyl ketones, and secondary alcohols) can participate in the haloform reaction. So may olefinic substances (general structure, $CH_3CH{=}CR_1R_2$), which will be oxidized by hypochlorous (HOCl) first to secondary alcohols and then to methyl ketones. The site of attack by chlorine is the carbon adjacent to the one bearing oxygen, and this attack, wherein the hydrogen atoms are successively replaced by chlorine, is preceded by a dissociation of one hydrogen (as H^+) to produce a carbanion ($-CH_2^-$) that can react with Cl(I), from hypochlorous acid. Chlorine substitution continues until all hydrogen atoms on the same carbon have been replaced. The final step involves a hydrolytic cleavage of the trihalogenated carbon (the trichlorinated carbon, in this example) to form the THM, which in this example would be chloroform (Morris, 1975).

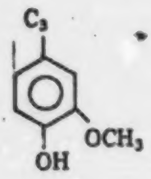
While it is well known that compounds containing acetyl groups are reactants in the haloform reaction, methyl ketone (acetone, CH_3COCH_3) itself is not a likely precursor during water treatment. According to Morris and Baum (1978), who cited a study by Bell and Lidwell (1940), the half-life for chloroform formation from acetone at pH 7 and room temperature is nearly a year. Stevens et al. (1978) also discounted acetone as a precursor of THM because of the slow reaction rate. The rate-limiting step in the haloform reaction is the ionization that produces carbanions, and, apparently, simple ketones are not representative of those which react quickly to produce chloroform under conditions in water treatment plants. Studies with model compounds, which are discussed in the section pertaining to chlorine chemistry, have shown that other types of compounds, including other ketones, may react more rapidly than the simple ketones.

Humic Substances

As was mentioned previously, it is an attractive assumption that naturally occurring humic substances, which are derived from the structural components of living and decaying plants and/or soil dissolution and runoff, provide the most ubiquitous source of haloform precursors in natural water systems. Only limited information is available concerning the structure of these complex natural products, and it is not yet known whether all the _major_ structural features have been identified, if any structural differences exist among the humic substances in waters from different geographic areas and if these substances are closely or distantly related to soil humic and marine humic materials.

The term "humic acid" is generic and refers to that fraction of soil organic material that is soluble in alkaline solutions but insoluble in acid and ethyl alcohol (Christman and Oglesby, 1971). The fraction that is soluble in acid is commonly labelled "fulvic acid," and that material precipitated by acid but soluble in ethyl alcohol is "hymatomelanic acid." Soils vary widely in their relative compositions of these acids, but aquatic organic material behaves operationally as fulvic acid (Black and Christman, 1963), which typically contains more oxygen and less nitrogen than the humic acid fraction in both soil and aquatic organic matter. Marine organic matter (including sedimentary material) is derived largely from marine organisms and contains more sulfur than its fresh water equivalent (Nissenbaum and Kaplan, 1972; Stuermer and Harvey, 1978). Christman and Oglesby (1971), Steelink (1977), Schnitzer and Kahn (1972), and Dubach _et al_. (1964) have reported the presence of carboxyl, phenolic and alcoholic hydroxyl, carboxyl, and methoxyl functional groups in humic material. It would appear that the more oxygenated fulvic acid fraction has a greater carboxyl acidity than the humic acid fraction.

Whittaker and Likens (1973) estimated that 90% of the terrestrial biospheric carbon (standing biomass) is tied up in woody tissue. Lignin is a dominant (20%-40%) chemical entity in woody tissue. Because of its refractory nature, it is probably a principal precursor of soil humus, although a myriad of other natural products unquestionably contribute to the complex pool of soil organic matter. Lignin itself is a mixed polymer of guaiacyl (I), syringyl (II), and p-hydroxyphenylpropane (III) aromatic moieties:



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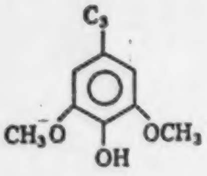

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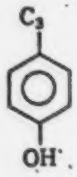

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No other substitution patterns are known in nature and no other length of alkyl side chain has been found in lignin from any source. Oxidative degradation of lignin produces, therefore, only three aromatic substitution patterns (I, II, and III), although the relative amounts of each vary among the gymnosperms, angiosperms, and the grasses. Intermonomeric linkages in the lignin macromolecule are of both carbon-to-carbon and ether linkage types. The largest single contributor is believed to be the β-4' ether configuration. Side-chain carbon atoms may be in various states of oxygenation or unsaturation, and may contain methyl ketone, allyl, and secondary alcohol configurations.

Significant changes occur in the humification process as reflected by comparative functional group data for lignin and soil humic acid (Table 1).

This process, which is oxidative in nature, may strongly affect the characteristics of aquatic humic material. Microbial mediation is apparent when there is a marked decrease in methoxyl group and increases in phenolic hydroxyl and carboxyl acidity.

The contribution of woody tissues to marine humus is not apparent from the results of degradative experiments on marine fulvic acids, which are considered to be autochthonous materials. Degradation of both soil humic acid and aquatic humic material reflects a partial lignitic origin (Table 2), although a variety of other aromatic patterns (m-dihydroxy) and aliphatic chain lengths (C_2-C_{17}) must result from other natural product sources. The data in Table 2 indicate key areas of inadequacy in our knowlege of the chemical nature of aquatic humic substances. It is not possible to model natural aquatic humic material with a desirable degree of chemical accuracy, and it certainly is not possible to state that THM's, which appear in chlorinated water containing humic substances, are derived by the classic haloform reaction.

Table 1. Comparative Functional Group Analysis of Soil Humic Acid and Spruce Lignin[1]

	Group Content, in mM/g	
Functional Group	Lignin	Soil Humic Acid
Methoxyl	5.1	0.2
Total Hydroxyl	6.2	5.1
Phenolic Hydroxyl	1.6	2.9
Alcoholic Hydroxyl	4.6	2.2
Carbonyl	1.0	5.5
Carboxyl	Trace	86.

[1] From Christman and Oglesby, 1971

TABLE 2. Chemical Degradation Products of Humic Substances

Technique	Marine Humus[1]	Soil Humus[2]	Freshwater Humus[3]
Acid hydrolysis	(FA) 9 amino acids (Gagosian and Stuermer, 1977) (FA) 20% organic soluble (not identified)	20 amino acids (Kahn and Sowden, 1972) peptides, sugars, phenolic carboxylic acids (trace)	No amino acids (Gjessing, 1976)
Alkaline hydrolysis	No data	(HA) 11% aliphatic (C_{16}-C_{18}) fatty acids 7% phenolic acids (principally quaiacyl and syringyl) 2% polycarboxylic aromatic acids (Neyroud and Schnitzer, 1975)	(HA) phenols, phenolic acids (including quaiacyl and syringyl) aliphatic acids (C_{13}-C_{17}) and citric acid (Christman, 1978a)
Oxidation	Conversion to carbon dioxide and water noted with strong oxidants. (Limited experimental data) (Stuermer and Harvey, 1978).	Alkaline cupric oxide: (HA) vanillin, p-hydroxybenzaldehyde, syringaldehyde, p-hydroxybenzoic acid, vanillic acid, 3,5-dihydroxybenzoic acid, m-hydroxybenzoic acid (Green and Steelink, 1962) Alkaline potassium permanganate: aliphatic monocarboxylic acids (C_2-C_6) and dicarboxylic acids (C_2-C_8), phenolic acids, and benzene polycarboxylic acids (including methoxy-substituted analogs) (Schnitzer and Kahn, 1972)	Alkaline cupric oxide: (HA) vanillin p-hydroxybenzaldehyde, syringaldehyde, p-hydroxybenzoic acid, vanillic acid, 3,5-dihydroxybenzoic acid (Christman and Ghassemi, 1966). Alkaline potassium permanganate:aliphatic monocarboxylic acids (C_7-C_{15}) and dicarboxylic acids (C_1-C_{15}), phenolic acids, and benzene polycarboxylic acids (including methoxy-substituted analogs) (Christman, 1978b)
Reductive degradation	High pressure hydrogenation: n-alkanes (C_{12}-C_{26}, predominance of even carbon no.); alkyl benzenes (four homologous series, with side chains of C_{10}, C_{11}, and C_{12} predominant)	Zinc dust distillation: Polynuclear aromatic hydrocarbons (low yields) (Schnitzer and Kahn, 1972) Sodium-amalgam: p-hydroxybenzoic acid, vanillic acid, syringic acid, protocatechnic acid, quaiacyl and syringyl propionic acids, resorcinol, phloroglucinol, pyrogallol methylphloroglucinol, 2,6- and 2,4-dihydroxytoluene, and 3,5-dihydroxybenzoic acid Burges *et al.*, 1964)	No data

[1] FA/HA (Fulvic acid/humic acid) > 1.0 (Gagosian and Stuermer, 1977); HA + FA < 5% DOC (Dissolved Organic Carbon); autochthonous (Stuermer and Harvey, 1978)

[2] FA/HA variable

[3] FA/HA 1.0 (Black and Christman, 1963); % DOC variable; allochthomous (Shapiro, 1957)

[4] From total soil organic matter; acid hydrolysis has little effect on HA per se

The ultimate concern for public health protection is, of course, the fact that THM's are formed during the chlorination of drinking water sources. Consequently, a discussion of chemical mechanisms may appear to be rather academic. However, a precise understanding of the mechanisms by which the THM's are formed may prove to be truly beneficial by helping water utility personnel avoid the conditions during treatment that promote the appearance of high concentrations of these compounds in finished water. Studies with model compounds under well-defined laboratory conditions have been useful in elucidating these mechanisms and reaction conditions. Examples are given in the section pertaining to chlorine chemistry.

CHLORINE

Chlorine has been the principal disinfectant of community water supplies for several decades. Until recently, its use had never been questioned seriously because the health benefits derived from it were so obvious. Although an occasional taste-and-odor problem in finished water was attributable to the reaction of chlorine with some substance in the raw water, the events were usually intermittent, short-lived, and presumably did not affect the public health. However, in 1974, Rook (1974) in the Netherlands and Bellar et al. (1974) in the United States reported that chlorine reacts with organic precursors that are found in many source waters to produce a potential carcinogen, chloroform ($CHCl_3$).

In December 1974, Congress passed the Safe Drinking Water Act (PL 93-523), and in early 1975, the U.S. Environmental Protection Agency (EPA) began an 80-city water-supply survey--the National Organics Reconnaissance Survey (NORS)--to determine the extent of the problem (Symons et al., 1975). As part of NORS, finished waters from five cities (Miami, Florida; Seattle, Washington; Ottumwa, Iowa; Philadelphia, Pennsylvania; and Cincinnati, Ohio), which represented the major types of water sources in the United States, were analyzed as thoroughly as possible for all volatile organic compounds, i.e., those that can be stripped from solution by purging with an inert gas (Coleman et al., 1976). Seventy-two compounds were identified, 53% of them containing one or more halogens. A later study, the EPA National Organics Monitoring Survey (NOMS), included analyses of samples that had been taken from the water supplies of 113 cities (Brass et al., 1977) on four occasions over an 18-month period during 1976 and 1977. The source waters of a few cities were examined, but most of the effort was directed toward an analysis of finished waters for chloroform and 20 other volatile organic compounds. In addition to the 21 compounds that were orginally selected, five others appeared frequently and were reported.

Since 1974, there have been numerous other surveys similar to NORS and NOMS but they have been more restricted in scope. In addition, research activity has been intensified to isolate and identify the precursors, products, and mechanisms that are associated with the presence of potentially toxic organic compounds in both water and wastewater. In December 1976, the EPA published a list of 1,259 compounds that had been identified in a variety of waters (including industrial effluents) in Europe and in the United States (Shackelford and Keith, 1976). The agency is currently compiling a comprehensive register of all data concerning the identification of organic pollutants in water.

Properties of Aqueous Chlorine

Various aspects of chlorine chemistry have been reviewed by Jolley et al. (1978). Miller et al. (1978), Morris (1975, 1978), and Rosenblatt (1975). A synopsis of the basic principles will provide some understanding of the various forms that chlorine can assume in water and the reactions that it can undergo with certain types of compounds.

Reactive Forms of Chlorine in Water

"Aqueous chlorine" is a misleading term because the active form of chlorine that is present in treated water and wastewater is not the gaseous chlorine molecule (Cl_2) but, rather, a hydrolysis product, hypochlorous acid (HOCl), which is formed from the reaction between the chlorine molecule and water:

$$Cl_2 + H_2O = HOCl + H^+ + Cl^- \qquad (1)$$

Hypochlorous acid, a weak acid, can ionize as follows:

$$HOCl = H^+ + OCl^- \qquad (2)$$

The degree of ionization depends primarily on the pH and temperature of the water. The concentration of hypochlorous acid and the hypochlorite ion (OCl^-) are approximately equal at pH 7.5 and 25°C.

Another form of chlorine, the hypochloronium acidium ion (H_2OCl^+), is known to exist (Miller et al., 1978; Rosenblatt, 1975), but its concentration would be extremely low in water at pH's between 5 and 9. Still another form of chlorine, the chloronium (or chlorinium) ion (Cl^+) has been proposed as an important reactant in aqueous solutions of organic compounds (Carlson and Caple, 1978), although its existence is disputed (Rosenblatt, 1975). Nevertheless, Morris (1978) pointed out that "the reactant behavior of HOCl with organic carbon and amino nitrogen is as an electrophilic agent in which the chlorine atom takes on partially the characteristics of Cl^+ and combines with an electron pair in the substrate." Finally, Carlson and Caple (1978) mentioned that another form of chlorine, the chlorine radical (Cl) may react in the light to produce chlorine-substituted organic compounds when the parent chlorine molecule is not lost by any other significant reaction pathway. Rosenblatt (1975), citing others, described this form as "probably the most selective chlorinating species of all."

Free chlorine species (HOCl, OCl^-, Cl_2, H_2OCl^+, Cl^+) will oxidize both the bromide ion (Br^-) and iodide ion (I^-) to hypobromous and hypoiodous acids (HOBr and HOI). This reaction, as will be discussed later, is postulated to account for the presence of bromine- and iodine-substituted organic compounds, particularly the mixed-halide haloforms, in waters that had been disinfected by chlorination.

Reactions of Hypochlorous Acid With Organic Compounds

Chlorine reacts in solutions of organic compounds by one or more of three basic mechanisms (Jolley *et al.*, 1978; Miller *et al.*, 1978; Morris, 1975; Morris, 1978), namely, addition, during which chlorine atoms are added to a compound; oxidation; and substitution, during which chlorine atoms are substituted for some other atom that is present in the organic reactant. All three of these reactions involve hypochlorous acid as an electrophile.

Only addition and substitution reactions produce chlorinated organic compounds. Oxidation reactions account for most of the "chlorine demand" of natural waters and waste treatment effluents (Jolley *et al.*, 1978; Morris, 1975), but the end products are not chlorinated organic compounds. That is not to say that those products cannot be harmful. Miller *et al.* (1978) have mentioned that epoxides can be produced from carbon-chlorinated compounds at pH values that are common in water treatment plants (e.g., pH 9.5-10.5) where softening is practiced. To illustrate, they describe the reaction between ethylene (C_2H_4) and hypochlorous acid, which yields ethylene chlorohydrin ($ClCH_2CH_2OH$) as an intermediate. This hydrolyzes to form the epoxide, ethylene oxide (C_2H_4O). Carlson and Caple (1978) mentioned one such reaction, in which a mixture of chlorohydrins resulted from the reaction of oleic acid [$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$] with hypochlorous acid.

Presumably, these would be converted to epoxides if the pH were to be increased. Carlson and Caple also showed how a ubiquitous natural compound, α-terpineol [$CH_3 \bullet C_6H_4 \bullet C(CH_3)_2)OH$], could form epoxides when reacted with hypochlorous acid. These reactions illustrate how chlorination may result in the development of non-chlorinated products, e.g., the epoxides, which may pose health risks. In instances such as those just discussed a chlorinated intermediate, which itself should be evaluated toxicologically, is involved.

Chlorine By-Products Found in Drinking Water and Selected Nonpotable Waters

The most frequently mentioned products of aqueous reactions between chlorine and selected types of organic compounds are discussed in this section. Special attention is given to the trihalomethanes (THM's) because of the current interest in them as potentially hazardous by-products of chlorination in municipal water treatment facilities. The specific reactions by which THM's are produced in chlorinated natural waters are not well understood because the chemical structures of the precursor organic compounds, which are thought to be primarily humic substances, are highly varied and extremely complex. A summary of the relevant facts concerning these ubiquitous, natural organic substances is presented in the section on precursors. The term "haloform reaction" is often mentioned as the mechanism by which THM's are produced when natural waters are chlorinated. This has not been validated definitively in actual water treatment systems. However, the reaction will be discussed in conjunction with THM formation in natural waters because it is one possible mechanism that has been described thoroughly in the literature.

Other products of chlorination that are discussed below include the chlorinated phenols, which have been of concern primarily because they impart offensive tastes to drinking water, and compounds that have been isolated during carefully controlled experiments involving analyses of both chlorinated and unchlorinated samples of freshwater and its analogs. Data derived from in-plant studies are difficult to interpret because raw waters are seldom uniform in composition over time, especially surface waters and raw sewages. Thus, there is always some unavoidable uncertainty as to whether compounds that have been isolated from finished waters were produced by chlorination of precursor organic compounds in the influent or whether they were present before the influent entered the plant. Despite the uncertainty, some published in-plant studies are described in this section. Those related to THM formation are especially noteworthy. Abundant laboratory evidence shows that the high concentrations of THM's that have been observed in many finished drinking waters are produced by reactions between chlorine and precursor organic compounds that are commonly found in natural waters.

Trihalomethanes

The current interest in THM's was prompted by the reports of Rook (1974) and Bellar et al. (1974), which linked the presence of chloroform and other trihalogenated derivatives of methane (CH_4) in finished drinking water to the chlorination of raw waters during treatment. Rook (1974) demonstrated that THM's were produced by the chlorination of aqueous extracts of peat, and he postulated that the precursors were the humic substances. The presence of THM's in laboratory-chlorinated waters that had been taken from a lake in a "peaty region" helped confirm Rook's hypothesis. Later laboratory studies involving the chlorination of aqueous solutions of humic substances (e.g., Babcock and Singer, 1977; Hoehn et al., 1978; Stevens et al., 1976) further confirmed Rook's hypothesis. Bellar et al. (1974) reported that THM concentrations in Ohio River water increased as it was being treated and chlorinated at several points in the Cincinnati, Ohio waterworks. Rook (1974) reported similar observations for treated water from the Rhine and Meuse Rivers at the Berenplaat treatment plant in the Netherlands.

The prevalence of THM's in U.S. municipal water supplies was demonstrated by the NORS survey in 1975 and the NOMS survey in 1976. According to Symons et al. (1975), the total THM (TTHM) concentrations in the 80-city survey (NORS) were log-normally distributed, while chloroform appeared in the highest concentrations (median, 21 μg/l), followed by bromodichloromethane ($CHCl_2Br$) (median, 6 μg/l) and lesser concentrations of chlorodibromomethane ($CHBr_2Cl$) and tribromomethane ($CHBr_3$). The distributions are shown in Figure 1. Brass et al. (1977) reported median concentrations of chloroform and bromodichloromethane of 27 and 10 μg/l, respectively, in the 113 supplies that were surveyed during the first phase of NOMS. During that phase, sampling and handling procedures were identical to those used during NORS. The THM concentrations in the raw water sources, which included rivers, ground waters, and lakes, were much lower. Hoehn et al. (1977) and Hoehn and Randall (1977) reported results of an extensive 2-year THM monitoring program at a water treatment plant and at the distribution system of a Northern Virginia water supply that was supplied by a reservoir. Mean finished-water THM concentrations varied seasonally and were from one to two orders of magnitude greater than those found in the source water. Average chloroform concentrations in finished drinking water were from five to 10 times greater than the median reported for NORS and NOMS, but concentrations of bromodichloromethane were comparable.

As was mentioned earlier, it is difficult to determine whether many organic compounds that are recovered from

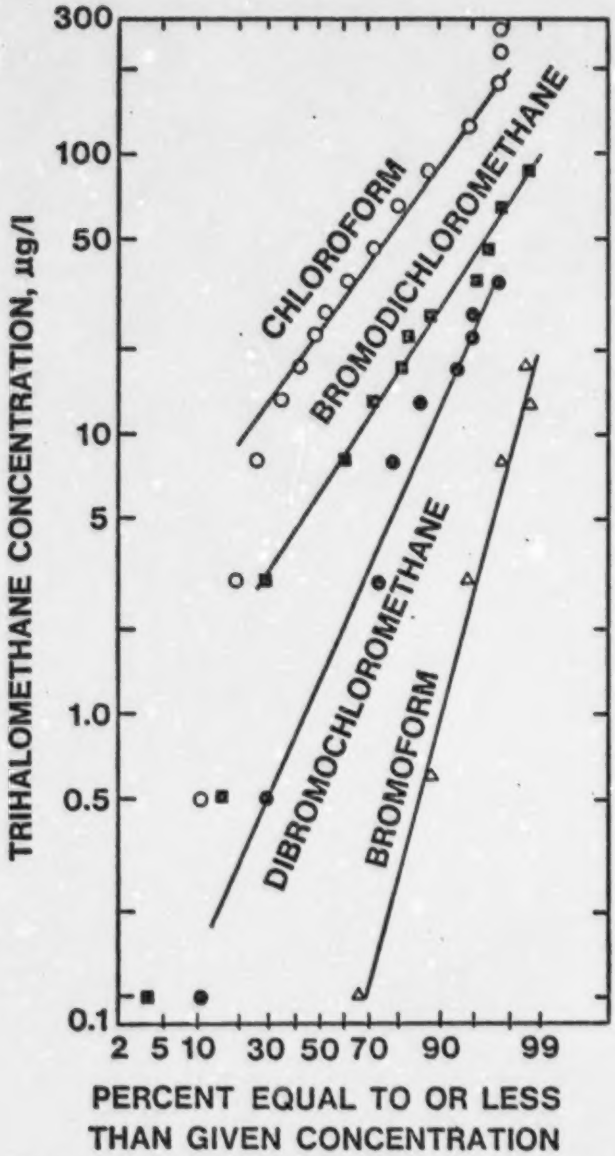

Figure 1 Frequency distribution of trihalomethane data (NORS). (Stevens *et al.*, 1975)

finished waters during in-plant studies actually were formed during the treatment process, especially when analyses of intermittently collected "grab" samples provide the data base. The uncertainty factor is greater when compounds are seldom recovered from finished water and when they are occasionally detected in untreated water at concentrations that are similar to those found in treated water. In these instances, the origin of a substance that has been isolated from finished water would be determined more accurately by a comparative analysis of samples from both influent and effluent water that has been collected and composited for a period at least equal to the hydraulic detention time within the plant. In the in-plant surveys, the attribution of THM's to chlorination is more certain although grab samples were used, primarily because THM's have often been found in finished waters in much higher concentrations than in the untreated influent waters.

Mention has already been made of the fact that mixed-halide THM's have been identified on numerous occasions, the most common ones being the bromochloromethanes, $CHCl_2Br$ and $CHClBr_2$. These, and occasionally iodine-containing, mixed-halide THMS's, have been reported but in much lower concentrations than chloroform. The mechanisms that are involved in the formation of these compounds during chlorination are discussed in the bromine-iodine section of this report. Fluorinated isomers are not expected to be produced by these mechanisms (Kleopfer, 1976).

The production of chlorinated THM's in concentrations that are typical of those reportedly recovered from finished drinking waters is dependent upon the initial presence of free chlorine. Thus, unnitrified, chlorinated sewage effluents that contain no free chlorine usually contain low (<10 μg/liter) THM concentrations (Stevens et al., 1978) unless industrial wastes containing THM's are discharged into the sewers. The reason for this phenomenon is that free chlorine species react extremely rapidly with ammonia (NH_3) (Morris, 1967), which is present in sewage in concentrations of parts per million. Under those conditions the concentration of free chlorine is extremely low (Jolley et al., 1976).

Nonhaloform Products of THM Reactions

While it is not certain that the classic haloform reaction is solely responsible for the appearance of THM's in chlorinated drinking water, it illustrates the fact that organic compounds other than THM's are formed as a natural consequence of reactions involving carbanions that lead to THM formation. Some of these compounds are chlorinated intermediates, while others are terminal products that are formed simultaneously with the THM's. For example, if the classic haloform reaction (involving a ketone) is operative, a carboxylic acid is formed during the final hydrolysis step which results in the production of a THM:

$$\mathrm{R\text{-}C\text{-}CCl_3 + H_2O \text{ ---> } R\text{-}C\text{-}OH + CHCl_3}$$

Nonhalogenated products, which may contain aromatic or alicyclic structures (e.g., benzene rings or cyclic hydrocarbons, respectively), should not be ignored when assessing potential health risks that are associated with water chlorination.

Another fact to consider is that if the free THM were not produced (e.g., by hydrolysis, in the haloform reaction), some chlorinated intermediate containing a chlorinated methyl group might be present. Suffet _et_ _al_. (1976) have reported finding 1,1,1-trichloroacetone (Cl_3CCOCH_3) in two different potable water supplies near Philadelphia. One water treatment plant is on the Delaware River; the other is on the Schuylkill River. The 1976 EPA Survey (Shackelford and Keith, 1976) reported no instances of trichloroacetone in rivers, lakes, or groundwaters. Trichloroacetone is readily hydrolyzed at a pH above 5 (Suffet _et_ _al_., 1978, private communication). Suffet _et_ _al_. (1976) utilized two different on-line composite isolation methods with dechlorination and adjustment to pH 4 to stabilize the compound. They isolated it with a XAD-2 resin and continuous liquid-liquid extractor. This compound is a likely intermediate in the haloform reaction, especially when acetone (C_3H_6O) is present in the river water. The haloform reaction for acetone is extremely slow (Bell and Lidwell, 1940; Morris and Baum, 1978). Trichloroacetone hydrolysis is much quicker. To be observed, the compound must be extracted immediately or the pH must be lowered to ≤4 to stabilize it.

Morris and Baum (1978) reported that trichloroacetate (CCl_3COO^-) and hexachloroacetone (CCl_3COCCl_3) are possible intermediates of the classic haloform reaction, but they argued that substantial quantities of other chlorinated organic compounds, except chloroform, should not be formed. Obviously, the formation of chlorinated intermediates other than these could occur by mechanisms other than the haloform reaction.

Pfaender _et al_. (1978) presented corroborating evidence that trichlorinated intermediates do occur in chlorinated waters. They detected more chloroform in water samples that had been analyzed by direct aqueous injections (DAI) of samples into a gas chromatograph than by a conventional technique that involves stripping the volatile THM's from solution with an inert purge gas. They attributed the higher recoveries to thermal decomposition of nonvolatile, chlorinated intermediate compounds that had been introduced into the analytical instrument by DAI but which remained in solution during the analysis involving the purge technique. They did not identify any of the intermediates but did show that chloral (CCl_3CHO), a previously suspected intermediate, was stable under the conditions of the anlaysis by DAI and could not account for the observed increases in chloroform concentration.

Carbon tetrachloride (CCl_4) is not produced during the haloform reaction, nor should it be produced by any other mechanism involving electrophilic substitution of chlorine on a carbanion. Shackelford and Keith (1976) reported its presence in finished drinking water on numerous occasions when it had not been detected in the untreated water. The most likely source of carbon tetrachloride in these instances is the chlorine itself. Carbon tetrachloride and hexachloroethane (C_2Cl_6) have been identified as contaminants of the chlorine manufacturing process (Laubusch, 1959). Hexachlorobenzene (C_6Cl_6) has also been identified as a contaminant (Blankenship, 1978).

Reactions Involving Phenolic Substances

The primary concern with phenolic compounds in drinking water supplies has been the offensive tastes that result from their reaction with hypochlorous acid. The presence of the hydroxyl group on the benzene ring activates the ring and permits chlorine to substitute readily. Multiple substitutions can lead to rupture of the parent ring (Burttschell et al., 1959). Morris (1975) has provided a good overview of the available literature of the subject, including that related to the products that have been observed after rupture of the ring. Lee and Morris (1962) and Lee (1967) have described in detail the kinetics of phenol chlorination and have recommended controls for the taste and odor problem that is caused by chlorophenols.

Phenolic substances that are present in natural waters are highly varied. Reactions produced in the laboratory with the simple phenols may not occur when the more complex phenols are present. Therefore, conclusions that are derived from these laboratory studies should be extended with caution to systems that contain the more complex and diverse forms of phenols that exist in nature.

Reaction Products From Chlorinated Surface Waters and Sewage Effluents

Because of the difficulties of interpreting in-plant studies involving analyses of influent and effluent grab samples, most of the investigations discussed below are limited to those involving analyses of pairs of influent water or sewage samples that differed only in that one of each pair was chlorinated in the laboratory. Despite the uncertainties that are associated with data from influent-effluent analyses, a few investigations involving in-plant studies have been reviewed either because the compounds that were detected in the chlorinated effluents were seldom, if ever, detected in untreated waters or because the study involved a broad survey of many treatment facilities.

Products from Chlorinated Surface Waters

Jolley et al. (1978) chlorinated surface sources that were used to cool water at two Tennessee electric power generating facilities, one in Kingston (Watts Bar Lake) and the other near Memphis (Mississippi River). Radioisotopic ^{36}Cl in $HO^{36}Cl$, was applied in dosages of 2.1 mg/l at Kingston and 3.4 mg/l at Memphis, and was allowed to react for 75 and 15 minutes, respectively. The waters were concentrated by vacuum distillation and compounds were separated for analysis with a scintillation counter by high-pressure liquid chromatography (HPLC). Chlorination yields (as Cl) of chloroorganic constituents that were separated by HPLC were 0.5% at Kingston and 3.0% at Memphis. A variety of compounds was recovered. The influent water was not analyzed because the presence of the ^{36}Cl isotope in the molecules indicated that the product was derived from the chlorination. There was no attempt to confirm the identity of the reported compounds by gas chromatography/mass spectroscopy analysis.

Among the chlorinated compounds that were recovered in concentrations ranging from a few tenths of a part per billion (ppb) to as high as 20 ppb were a nucleoside, three purines, a pyrimidine, seven aromatic acids, and five phenolics. The Mississippi River sample from Memphis contained the highest concentrations (0.7 to 20 ppb) because it contained less ammonia--hence more free chlorine to serve as the active oxidizing agent. The analytical methods recovered only nonvolatile, or slightly volatile compounds, and did not permit detection of large polymeric substances such as humic acids or nucleic acids. The pyrimidine, 5-chlorouracil, which was present at concentrations of 0.6 and 7 ppb in the two samples, has captured attention because it could be incorporated into cellular genetic material (Jolley et al., 1978; Gehrs and Southworth, 1978). Gehrs and Southworth (1978) commented that one of the chlorophenols, 4-chlororesorcinol [ClC_6H_3-1,3-$(OH)_2$], was potentially toxic, but they made no mention of the possible impacts of the other chloroderivatives that were recovered.

In a study of chlorinated (2.0 mg/l, 68 hour contact time) and unchlorinated waters from Lake Zurich, Giger et al. (1976) recovered several α-chloroketones and a variety of THM's that contained chlorine, bromine, and iodine, all of which were absent in the unchlorinated control sample. The ketones included 2,2-dichlorobutanone ($CH_3CCl_2COCH_3$), 2,2-dichloropentan-3-one ($CH_3CCl_2COC_2H_5$), 1,1,1-trichloroacetone (also recovered by Suffet et al., 1976), and 3,3-dichlorohexan-4-one ($C_2H_5CCl_2COC_2H_5$). In addition, they detected minor quantities of chlorinated alkylated benzene compounds. The α-ketones and THM's were identified by mass spectrometry.

Brass et al. (1977) mentioned that two sets of raw and finished waters from an unidentified city were analyzed for volatile organics during NOMS Phase III. They observed that aromatic compounds (unspecified) were found in finished water but not in the raw water samples. Further work was anticipated. A later publication concering NOMS-III (Munch et al., 1977) lists the relative recoveries of 25 various organic compounds from the raw and finished waters at 11 locations. Compounds other than THM's, which were recovered more often in finished waters than in raw, included benzene (C_6H_6) (4 vs 0), chlorobenzene (C_6H_5Cl) (3 vs 1), ethylbenzene ($C_6H_5C_2H_5$) (3 vs 0), dichloromethane (CH_2Cl_2) (3 vs 0), toluene ($C_6H_5CH_3$) (3 vs 1), and a xylene isomer ($C_6H_4(CH_3)_2$) (4 vs 1). (Compounds where the difference in recoveries was only one are not listed). The ranges of concentrations that were observed when the compounds were quantified included: 0.58-6.1 µg/l for chlorobenzene, 0.1-1.5 µg/l for benzene, 0.42-0.57 µg/l for ethylbenzene, and 0.48-19 µg/l for toluene. The means were 2.7, 0.88, 0.50, and 6.9 µg/l, respectively.

Products from Chlorinated Sewage Effluents

Jolley (1975) chlorinated primary- and secondary-treated sewage effluents with various forms of ^{36}Cl-tagged chlorine compounds to determine which chlorination products could be found. Chlorine was dispensed as a gas at dosages and contact times that were similar to those expected in actual plant operations. Additional experiments were performed in the laboratory wherein a ^{36}Cl-tagged hypochlorite solution was used as the chlorinating agent. Of the 44 compounds that were recovered, 17 mentioned previously as having been recovered from cooling waters were identified in the sewage effluents. Less than 1% of the chlorine could be accounted for within organic compounds. Most of it was in the form of chloride ion (Cl^-), indicating that most of the chlorine that is applied to sewage serves as an oxidant. There are many difficulties inherent in the separation and identification of compounds in waters that are heavily laden with organic and inorganic contaminants. It may be that more chloroorganics were present than could be recovered. However, this possibility does not alter the basic conclusion that most of the chlorine is simply reduced to chloride ion during the oxidation of sewage constituents. Nevertheless, the oxidized organic compounds have importance from an environmental perspective whether or not they contain chlorine.

Garrison _et_ _al_. (1976) identified extractable volatile organics in lime-clarified, tertiary-treated sewage from the Blue Plains pilot plant near Washington, D.C. Chlorination was effected by sodium hypochlorite (NaOCl), which was added to achieve breakpoint and a final, free residual of 3 to 5 mg/l. The final pH was between 7.0 and 7.5. Samples were extracted and fractionated by standard analytical procedures, then concentrated and methylated before analysis. The most pronounced effect of the chlorination was evidenced by the appearance of chlorocyclohexane

($C_6H_{11}Cl$) and tetra-, penta-, and hexachloroethanes ($C_2H_2Cl_4$;C_2HCl_5;C_2Cl_6) in the effluent. None of the compounds was quantified.

These compounds are unusual constituents of chlorinated waters. The pentachloroethane is not an ordinary commercial material and, therefore, would probably not have an industrial origin. Commenting on his previous work (Garrison *et al*. 1976), Garrison (1978) provided some insight concerning the appearance of these compounds. Studies at the EPA Laboratory in Athens, Georgia have shown that cyclohexene (C_6H_{12}) is a common contaminant of methylene chloride (CH_2Cl_2), which is used as the extracting solvent. If the aqueous system being extracted contained residual chlorine, the cyclohexene could be converted to 1,2-dichlorocyclohexane by the addition of chlorine to the double bond. During the original study, the solvent may have contained other alkene impurities that could have reacted with chlorine to form the tetra-, penta-, and hexachloroethanes, but that possibility was not explored. If those impurities had existed, they would have been masked during analysis by the methylene chloride peak on the gas chromatogram since they are highly volatile substances. No "blanks" (control tests) were analyzed because the possible problem was not recognized. Moreover, both raw and treated sewages were being analyzed and the differences in composition were of prime interest. However, Garrison (1978) emphasized that these chlorinated aliphatic compounds, although unusual, have been identified in studies subsequent to the one reported in the 1976 publication.

Glaze et al. (1976, 1978) and Glaze and Henderson (1975) reported the appearance of 38 compounds that were generated by superchlorination (2,000 mg/l) of sewage effluent that had received secondary treatment. Most of the chlorinated compounds that were identified were aromatic derivatives. Many of them involved aromatics with no activating substituent groups. Among those that appeared were the chloroderivatives of benzene, toluene, and benzyl alcohol ($C_6H_5CH_2OH$) and the nonaromatic derivatives such as chlorocyclohexane (reported also by Garrison et al., 1976), a chloroalkyl acetate, and three chlorinated acetone derivatives (tri-, penta-, and hexachloroacetone). The acetone derivatives may be precursors of chloroform (see also Suffet et al., 1976). According to the authors, they may have been produced by an acid-catalyzed reaction between acetone and chlorine.

Glaze and Henderson (1975) and Glaze et al. (1976, 1978) also reported that an increase in the concentration of chlorine-containing compounds, as estimated by the Total Organic Chlorine concentration in nonpurgeable compounds, was observed in the sewage as the chlorine dose was increased from 25 to 2,000 mg/l. The TOCl concentration increased from 80 to 906 µg/l but decreased to 164 µg/l when the chlorine dose was increased to 3,000 mg/l, thereby demonstrating the destruction of chloroorganic compounds that were formed at lower chlorine dosages. The chlorine that was bound in organic compounds accounted for less than 0.05% of the applied chlorine. The chlorine dosages far exceeded expected concentrations in routine sewage treatment plant operations. However, there are commercially available treatment units in which sewage and industrial waste sludges can be oxidized by superchlorination within the range of the high dosages used by Glaze _et al_. Superchlorination would probably be required to reduce the concentrations of chloroorganic compounds that increase when chlorine dosages are increased. Fuchs and Kuhn (1976) demonstrated a marked increase in concentrations of chlorinated organic compounds at a water treatment plant when Rhine River water was chlorinated to breakpoint. Activated carbon treatment reduced these concentrations, the removal ranging from 28% to 69% of the influent TOCl concentrations. Superchlorination was not attempted.

Sievers _et al_. (1978) found increased levels of aromatic hydrocarbons--such as toluene, xylenes, and styrene ($C_6H_5CH{=}CH_2$)--in chlorinated, secondary-treated wastewaters from the Metro-Denver sewage plant in District No. 1. Excess chlorine additions under laboratory conditions resulted in the formation of species of chlorotoluene ($ClC_6H_4CH_3$) and chloroxylene ($ClC_8CH_3(CH_3)_2$). No industrial discharges enter the system. Therefore, the authors believe that the precursors were not of industrial origin. Concentrations of these aromatics ranged from 0.1 to 2 ppb.

In the EPA survey (Shackelford and Keith, 1976), toluene was found in finished drinking waters on several occasions, although it has been detected also in river water. Garrison (1978) reported that recent studies by the EPA laboratories in Las Vegas, Nevada, show toluene to be present at concentrations up to 2 μg/l in pristine mountain streams in the Great Smoky Mountains National Park. The EPA investigators attributed this to automobile exhausts.

The EPA survey document also reported the frequent detection in finished drinking waters of the xylenes (ortho, meta, and para isomers) and, less frequently, styrene. These compounds were present in various raw water sources as well. Sievers _et al_. (1978) believed the precursors to be nonvolatile but did not postulate what they might be. According to them, toluene, styrene, and xylenes have been identified in 20 U. S. drinking water supplies and in certain Canadian supplies.

Chlorination of Model Compounds

Several recent publications have described the results of laboratory experiments involving chlorination of model compounds in aqueous solutions. The products have been reported and, in some instances, mechanisms were proposed. A select number of those publications are reported below.

Reactions Resulting in THM Formation

Rook (1976) presented evidence that diketones, which have been described as degradation products of fulvic acids (one component of humic substances) do produce chloroform more rapidly than simple ketones. He chlorinated 1,3-cyclohexanedione [$C_6H_8(=O)_2$], 5,5-dimethylcyclo-1,3-hexanedione [$(CH_3)_2C_6H_6(+O)_2$] (dimedone), and 1,3-indandione [$C_9H_5(=O)_2$] at concentrations (>200 mg/l Cl_2) that were high in comparison to dosages used in water treatment plants at pH 7.5 and 11 at 10°C. He obtained yields of chloroform ranging from 50% to 100% of the theoretical yields (0.5-1.0 moles of chloroform per mole of precursor) in 4 hours.

In a later publication, Rook (1977) reported that the yields of chloroform from a variety of hydroxylated compounds were quite high. Those producing the highest yields with relative low chlorine dosages were metadihydroxy compounds such as 1,3-benzenediol (resorcinol) [$C_6H_4(OH)_2$], 1,3-dihydroxynaphthalene [$C_{10}H_6(OH)_2$], and 3,5-dihydroxybenzoic acid [$HOOCC_6H_3(OH)_2$]. Resorcinol is known to be a degradation product of fulvic acids (Christman and Ghassemi, 1966). The hydroxyl groups are strongly "activating." Consequently, the carbon positioned between the two hydroxyl groups is activated from both sides, thereby becoming a strong carbanion, which is readily attacked by chlorine.

Rook (1977) pointed out that chloroform may be just one of many by-products of reactions between chlorine and these types of compounds. He mentioned that substitution, oxidative ring fissions, or even ring contractions and other fragmentations may occur. Christman et al. (1978a) also chlorinated resorcinol under laboratory conditions and found that the carbon between the hydroxyl substituents was removed from the structure, thereby producing a 1,2-diketocyclopentenedione (3-chloro-5,5-dichlorocyclopent-3-ene-1,2-dione). They also identified mono-, di-, and trichlorinated resorcinols that had been produced by simple substitution reactions. Additional work by Christman and coworkers is described below.

Morris and Baum (1978) chlorinated a variety of compounds that could produce reactive carbanions in solutions at pH 7 and 11. Several of the compounds contained the pyrrole ring, which exhibits active carbanion formation and is a component of many natural compounds such as the plant pigments chlorophyll and xanthophyll. The pyrrole ring is also present in tryptophane, proline (both amino acids), and indole, (a component of certain protein putrefaction products). They also studied a class of compounds that are described as "acetogenins," which also contain β-ketonic groups in structures that are common to natural pigments.

Other compounds that Morris and Baum investigated as possible haloform precursors were vanillin (4-hydroxy-3-

methoxybenzaldehyde and syringaldehyde (4-hydroxy-3,5,dimethoxylbenzaldehyde, both alkaline degradation products of woody materials. Neither compound has the 1,3-dihydroxy configuration that reacts rapidly to produce THM's. In some of the studies, the reactions with chlorine were permitted to proceed in near-neutral solutions for several hours. Then the pH was increased to between 9 and 11. While THM's were produced at the lower pH, greater concentrations were found when the pH was increased. Their major conclusion was that naturally occurring compounds, from which THM's can be produced, are capable of forming chlorinated intermediates as well at neutral pH as at high pH, and that only the final hydrolysis, which results in higher concentrations of THM's, is enhanced by elevated pH. They suggested that the hygienic quality of drinking water might best be monitored by measuring TOCl concentrations.

Christman et al. (1978b) have reacted several phenolic humic model compounds with hypochlorous acid in dilute aqueous solution. These models were selected on the basis of results from oxidative degradation of aquatic humic material. Their data (Table 3) suggest that aromatic substitution patterns that are typical of lignin and soil humic acid (1, 3, 5- and 1, 3, 4, 5-) produce less chloroform than the basic m-dihydroxy model (resorcinol). The decrease is particularly marked when hydroxy is absent or methylated. The yield data from the substituted cinnamic acid (3-phenyl-2-propenoic acid, $C_9H_8O_2$) indicate that the propyl side chain may be involved in the production of chloroform.

The yield of chloroform from resorcinol (Table 3) compares favorably with the data of Rook (1977). In addition, the configuration of the cyclopentene intermediate suggests that Rook's hypothesis concerning the location of the chloroform-producing carbon is correct.

Reactions Producing Compounds Other Than THM's

The previous section emphasized model compound studies that were designed primarily to elucidate the mechanisms of THM formation. This section contains a review of published data from investigators who were principally interested in chlorination products other than THM's.

Carlson et al. (1975) and Carlson and Caple (1978) addressed the problems of predicting the extent of chlorine incorporation into aromatic substances. They chlorinated aqueous solutions of a variety of compounds whose parent structure was the benzene ring but which contained a variety of substituent groups. Included in their studies were phenol (C_6H_5OH), anisole ($C_6H_5OCH_3$), acetanilide ($CH_3CONHC_6H_5$), toluene ($C_6H_5CH_3$), benzyl alcohol ($C_6H_5CH_2OH$), benzonitrile (C_6H_5CN), nitrobenzene ($C_6H_5NO_2$), chlorobenzene (C_6H_5Cl), methyl benzoate ($C_6H_5COOCH_3$), and benzene (C_6H_6) in concentrations of $9.5 \pm 0.6 \times 10^{-4}$ M. Chlorine (7.0×10^{-4} M) was added and allowed to react at

Table 3
Comparative Chloroform Yields for Some Humic Model Compounds[1]

Compound	Chloroform Yield, Moles of Chloroform/ Mole of Compound	Chlorine Demand, Moles of Chlorine/ Mole of Compound
1,3-dihydroxybenzene (resorcinol)	0.91 (30 min)	6.60
3,5-dihydroxybenzoic acid)	0.5 (40 min)	7.06
3,5-dimethoxylbenzoic acid	0.009 (40 min)	3.00
3,5-dihyroxytoluene (orcinol)	0.914 (30 min)	6.26
3,5-dimethoxy-4-hydroxybenzoic acid (syringic acid)	0.005 (40 min)	5.18
3,5-dimethoxy-4-hydorxycinnamic acid	0.0228 (40 min)	6.09
(3,5-dimethoxy-4-hydroxyphenyl) propionic acid	0.0959 (221 min)	7.79
3-methoxy-4-hydroxy hydrocinnamic acid	0.0149 (183 min)	5.55
3-methoxy-4-hydroxy cinnamic acid	0.184 (250 min)	8.44

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[1] From Christman *et al*. 1978b.

25°C for 20 minutes. Experiments were conducted at pH 3, 7, and 10. They also studied biphenyl ($C_6H_5C_6H_5$, the parent compound of polychlorinated biphenyls (PCB's).

As expected their results showed that phenol was the only aromatic compound with one substituent that reacted readily at pH's that are common to water treatment (e.g., pH 7 and 10). Others, like anisole and acetanilide, reacted to some degree, but only at pH 3. The substituent groups in anisole and acetanilide ($-O-CH_3$ and $-NH-CO-CH_3$, respectively) are not highly reactive with hydrochlorous acid at near-neutral pH's that are encountered in water treatment. Biphenyl reactions with chlorine under conditions that are normally found at water treatment plants were not significant. Either extremely long reacting times (days), high dosages of chlorine (>100 mg/l), or low pH's were required to obtain relatively small yields of the chlorinated biphenyls, but one or more of these conditions might prevail where superchlorination is practiced.

Inferences of Possible Chlorination By-Products

Inferences Regarding Polynuclear Aromatic Hydrocarbons

Polynuclear (or polycyclic) aromatic hydrocarbons (PAH's) are commonly found in water (Andelman and Snodgrass, 1974; Harrison et al., 1975), and many are known to be potent toxins, mutagens, and teratogens (Blumer and Youngblood, 1975; Hase and Hites, 1976). Blumer and

Youngblood (1975) concluded that PAH's that are found in recent sediments originate primarily from particulates that are produced by forest fires. But Hase and Hites (1976) presented data which they interpreted as evidence that PAH's in water are produced principally from urban air pollutants from man-induced combustion processes. Oyler *et al*. (1978) cited reports indicating that PAH concentrations can be reduced by aqueous chlorination reactions, resulting in the production of chlorinated napthalenes, a chlorobenzopyrene, and a benzopyrene quinone.

Oyler *et al*. (1978) also reported laboratory data indicating that PAH's are susceptible to conversion to "second-order" products in the presence of hypochlorite under conditions that are typical of those in water during disinfection. Specific data concerning chlorine doses were not given. Compounds that were recovered and quantified included anthraquinone (9,10-anthracenedione, $C_{14}H_8O_2$), and monochloro derivatives of fluorene ($C_{13}H_{10}$), phenanthrene ($C_{14}H_{10}$), 1-methyphenanthrene ($C_{14}H_9CH_3$), and 1-methylnaphthalene ($C_{10}H_7CH_3$). Several PAH's and their derivatives have been detected in finished drinking water (Shackelford and Keith, 1976). Therefore, one should not ignore the possibility that reaction products, similar to those that Oyler and his coworkers identified, can be formed during water chlorination.

Inferences Regarding Reactions with Biogenic Substances

Surface waters receive, through runoff, a variety of allochthonous materials other than humic substance that may be important reactants with chlorine during disinfection. The compounds number in the thousands, but few have been studied in detail. In addition to organic compounds that might be washed in, surface waters contain many compounds that are produced by actively growing (or decaying) algae and higher plants. Here, too, there is a myriad of possibilities. Most likely, it will not be practical to isolate, identify, and evaluate the potential toxicity of more than a few. Vallentyne (1957) has written a comprehensive review of the natural aquatic organic compounds.

Morris and Baum (1978) found that THM was produced from chlorophyll. Hoehn _et al_. (1978) observed a seasonal variation in finished-water THM concentrations during a 2-year study of a northern Virginia water supply. Their data suggested that the high THM concentrations that were observed during the summer months may have been related, at least in part, to the chlorophyll-a concentrations in the reservoir water near the raw water intakes of treatment plants.

Thompson (1978) and Barnes (1978) demonstrated that haloform yields from chlorinated extracellular products (ECP's) of actively growing algae were higher than those that have been reported for chlorinated humic substances. They showed that the THM yields of the organic compounds that dissolved in the culture medium were greater than those from either the living or decaying algal cells. Algal ECP's often account for a large fraction ($\leq$ 30%-35%) of the carbon that was fixed during photosynthesis. This can result in a variety of compounds including organic acids, especially glycolic ($HOCH_2COOH$), oxalic ($HOOCCOOH$), glyceric ($HOCH_2CH(OH)COOH$), and others; nitrogenous compounds, such as free amino acids and small peptides, which are produced in abundance by bluegreen algae (the cause of many nuisance conditions in reservoirs); carbohydrates, primarily as polysaccharides of reasonably high molecular weight, which are associated with sheaths and capsules; lipids, especially those with C_{16} and C_{18} fatty acids; and a variety of nucleic acids, vitamins, and "volatile substances", including 2-furaldehyde ($C_4H_3O{\bullet}CHO$), acetaldehyde (CH_3CHO), acetone (CH_3COCH_3), valeraldehyde [$CH_3(CH_2)_3CHO$], heptanal [$CH_3(CH_2)_5CHO$], and an odor constituent "geosmin" (1,10-dimethyl-trans-9-decahol). Barnes presented a comprehensive review of the literature pertaining to the organic compounds that have been identified as algal ECP.

Other biologically derived compounds that are ubiquitous in water are the terpenes and related compounds, which are produced in abundance by terrestrial plants, especially conifers. The chlorinated derivatives of α-terpenol, which were reported by Carlson and Caple (1978) and discussed above, are another example of natural organic compounds, which in the past virtually have been ignored in chlorination studies. Chlorination produces a variety of other compounds whose toxicity has not been evaluated.

Inferences Regarding Trichloroacetaldehyde

Keith et al. (1976) reported that trichloroacetaldehyde (CCl_3CHO, chloral) was found in the carbon-chloroform extracts (CCE) from six of the 10 city water supplies, which were selected for detailed organics analysis during NORS. Two of the cities in which chloral was found (New York and Seattle) secure their water from uncontaminated upland water supplies. Keith et al. concluded that although chloral is an industrial product, its appearance in the CCE from these two water supplies is strong evidence that the compound was produced in some manner by chlorination. Chloral in water forms chloral hydrate [$CCl_3CH(OH)_2$], which is a highly toxic hypnotic drug. It is highly soluble, therefore, it is not recoverable by the analytical methods that were routinely used during NORS, which involve purging volatile compounds from solution by an inert gas.

Bellar et al. (1974) postulated that both chloral and chloral hydrate would be formed as intermediates in the formation of chloroform by the chlorination of ethanol in aqueous solutions. Keith et al. (1976) did not propose this sequence of reactions as an explanation for the appearance of chloral in any of the city water supplies. They did corroborate data from earlier reports which showed that chloral hydrate decomposes to chloroform slowly. In test solutions, only about 2% of the compound hydrolyzed to form chloroform in 24 hours.

As mentioned previously, Pfaender *et al*. (1978) demonstrated that direct aqueous injection of chloral hydrate into a heated gas chromatogaph did not appreciably increase the recovery of chloroform. Therefore, while chloral does not appear to be a readily available source of chloroform in drinking water, its demonstrated presence and inferred relationship to chlorination indicate the need for further evaluation from a toxicological viewpoint.

CHLORAMINES

Combining ammonia (NH_3) with chlorine (Cl_2) to form chloramines for the treatment of drinking water has been called combined residual chlorination, chloramination, or the chloramine process. Objectives of this water treatment are to provide disinfecting residual which is more persistent than free chlorine in distribution systems and to reduce the unpleasant tastes and odors that are associated with the formation of chlorophenolic compounds (Symons *et al*., 1977). Thus, this process utilizes the formation of monochloramine (NH_2Cl) as indicated in the following reaction:

$$NH_3 + HOCl \longrightarrow NH_2Cl + H_2O \qquad (4)$$

The production of monochloramine is optimized by a pH range of 7 to 8 and a chlorine-to-ammonia ratio of 5:1 (by weight) or less (Symons *et al*., 1977). White (1972) states that the preferred ratio is 3:1 (by weight).

At higher chlorine-to-ammonia ratios or at lower pH values, dichloramine ($NHCl_2$) and trichloramine (NCl_3), also called nitrogen trichloride, are formed according to the following reactions:

$$NH_2Cl + HOCl \longrightarrow NHCl_2 + H_2O \qquad (5)$$

$$NHCl_2 + HOCl \longrightarrow NCl_3 + H_2O \qquad (6)$$

These and organic chloramines are produced during the chlorination of water containing ammonia or organic amines. Their presence may contribute to taste and odor problems in the finished water (Symons et al., 1977).

Ammonia may be added to the water before (preammoniation) or after (postammoniation) addition of chlorine. Preammoniation can prevent the formation of tastes and odors that are caused by reaction of chlorine with phenols and other substances. According to White (1972), postammoniation is the most often used ammonia-chlorine water treatment process.

The 1963 Inventory of Municipal Water Supplies (U.S. Public Health Service, 1963) indicated that only 308 of the 11,590 water treatment plants surveyed used an ammonia-chlorine process (Symons et al., 1977).

Properties of Chloramines Relevant to Drinking Water Treatment

Hypochlorous acid (HOCl) reacts rapidly with ammonia to form monochloramine, dichloramine, or nitrogen trichloride as shown in Reactions 4 through 6, respectively. The reaction products are dependent upon the pH, the relative concentrations of hypochlorous acid and ammonia, the reaction time, and the temperature (Morris, 1978).

Usually monochloramine is the only chloramine that is observed when pH values are greater than 8 and when the molar ratio of hypochlorous acid to ammonia is 1:1 or less.

At pH values less than 3, only nitrogen trichloride is ordinarily detected (Morris, 1978).

Drago (1957) described the general chemistry of monochloramine, and Theilacker and Wegner (1964) and Kovacic et al. (1970) reported its organic reactions in some detail. Most of these organic reactions occurred in nonaqueous media. Although extremely useful for organic syntheses, these experiments have only limited value for predicting effects from drinking water treatment.

Monochloramine has been the principal subject of several reviews. Its properties and chemistry have been described by Metcalf (1942), Colton and Jones (1955), Jander (1955a), Drago (1957), Theilacker and Wegner (1964), Czech et al. (1961), Gmelin (1969), and Kovacic et al. (1970). Monochloramine is a colorless, water-soluble liquid with a freezing point of minus 66°C. It may decompose violently above that temperature (Kirk-Othmer 1964, p. 914).

Relatively little is known about dichloramine. Chapin (1929) determined that its odor, volatility from aqueous solution, and relative solubility in various solvents are intermediate between those of monochloramine and nitrogen trichloride. He also found that dichloramine liberates iodine from acidified potassium iodide (KI) solution as do the other chloramines. Dichloramine solutions are reported to be unstable (Corbett et al., 1953; Palin, 1950). Recently, Gray and Margerum (1978) reported that aqueous dichloramine solutions are more stable than previously thought and, thus, may be more significant in the water treatment process.

Nitrogen trichloride is a bright yellow liquid with a strong irritating odor and lachrymatory fumes. Its melting point is below minus 40°C; its boiling point is 70°C. It is extremely explosive and, therefore, dangerous, except at very low concentrations. Its solubility in water is limited (Kirk-Othmer 1964, p. 916). In aqueous solutions it decomposes slowly to ammonia and hypochlorous acid (Remick, 1942). Corbett et al. (1953) observed that aqueous solutions of nitrogen trichloride are stabilized by small amounts of acid. The compound is an effective chlorinating agent, particularly in nonaqueous media (Dowell and Bray, 1917; Houben and Weyl, 1962; Jander, 1955b; Kovacic et al., 1970).

Monochloramine is the principal chloramine that is encountered under the usual conditions of water treatment. The rate of its formation, shown in Reaction 4, is extremely rapid at the concentrations and conditions of water treatment. At the pH range of most water supplies the reaction is usually 90% complete in approximately 1 minute. As shown in Figure 2, the reaction rate is maximum at pH 8.5 (Morris, 1978; Weil and Morris, 1949).

The specific rate of formation of dichloramine is much slower than that for monochloramine except at pH values less than 5.5 (Morris, 1978) (see Table 4). Because dichloramine forms much more slowly than monochloramine at near neutral

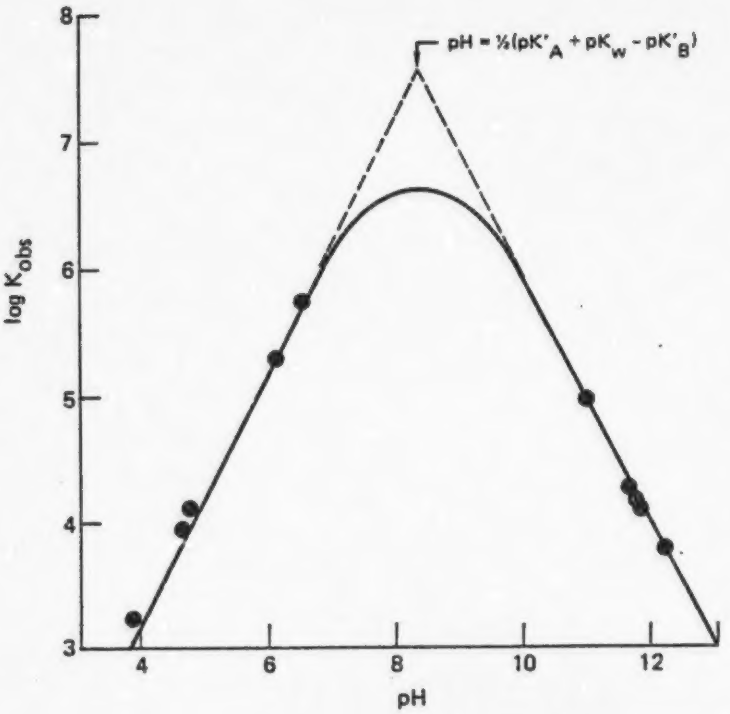


Figure 2 Variation in Rate of Chloramine Formation with pH. Calculated with log K_n = 8.48 (Morris, 1978)

pH values, dichloramine does not constitute a large percentage of the available chlorine unless the waters are quite acid or when the molar ratio of chlorine to ammonia is greater than one. The relative proportion of dichloramine and monochloramine for equimolar chlorine and ammonia and for 25% excess ammonia from pH4-9 are shown in Figure 3 (Morris, 1978). Dichloramine is much less stable than monochloramine or nitrogen trichloride. The decomposition of dichloramine is simplified in Reaction 7. The actual reaction is more complicated: more chlorine is reduced and some nitrate is formed (Morris, 1978).

$$2\ NHCl_2 + H_2O \text{ ---> } N_2 + HOCl + 3H^+ + 3Cl^- \qquad (7)$$

In acid solutions (pH 4 or less) or in solutions where chlorine concentrations far exceed those of ammonia, nitrogen trichloride is formed. Because nitrogen trichloride is formed from dichloramine, the reaction occurs only under conditions in which the dichloramine is reasonably stable. Thus, nitrogen trichloride is the only chloramine at pH values less than 3. At chlorine-to-ammonia molar ratios greater than 2, nitrogen trichloride occurs in diminishing proportions up to pH values of 7.5. Above pH 7.5, no nitrogen trichloride is found regardless of the ratio of chlorine to ammonia (Morris, 1978).

When chlorine is added to waters containing ammonia, the "breakpoint" phenomenon becomes significant in the pH range of 6 to 9. At chlorine-to-ammonia molar ratios of 0 up to

Table 4. Specific Rates for Chloramine Formation at 20°C[1]

Chloramine	k, M^{-1} sec^{-1}
Monochloramine[2]	5.6×10^6
Dichloramine[3]	2.7×10^2

[1] From Saguinsin and Morris, 1975.

[2] Assuming reaction between neutral molecules.

[3] For reactions not catalyzed by acid.

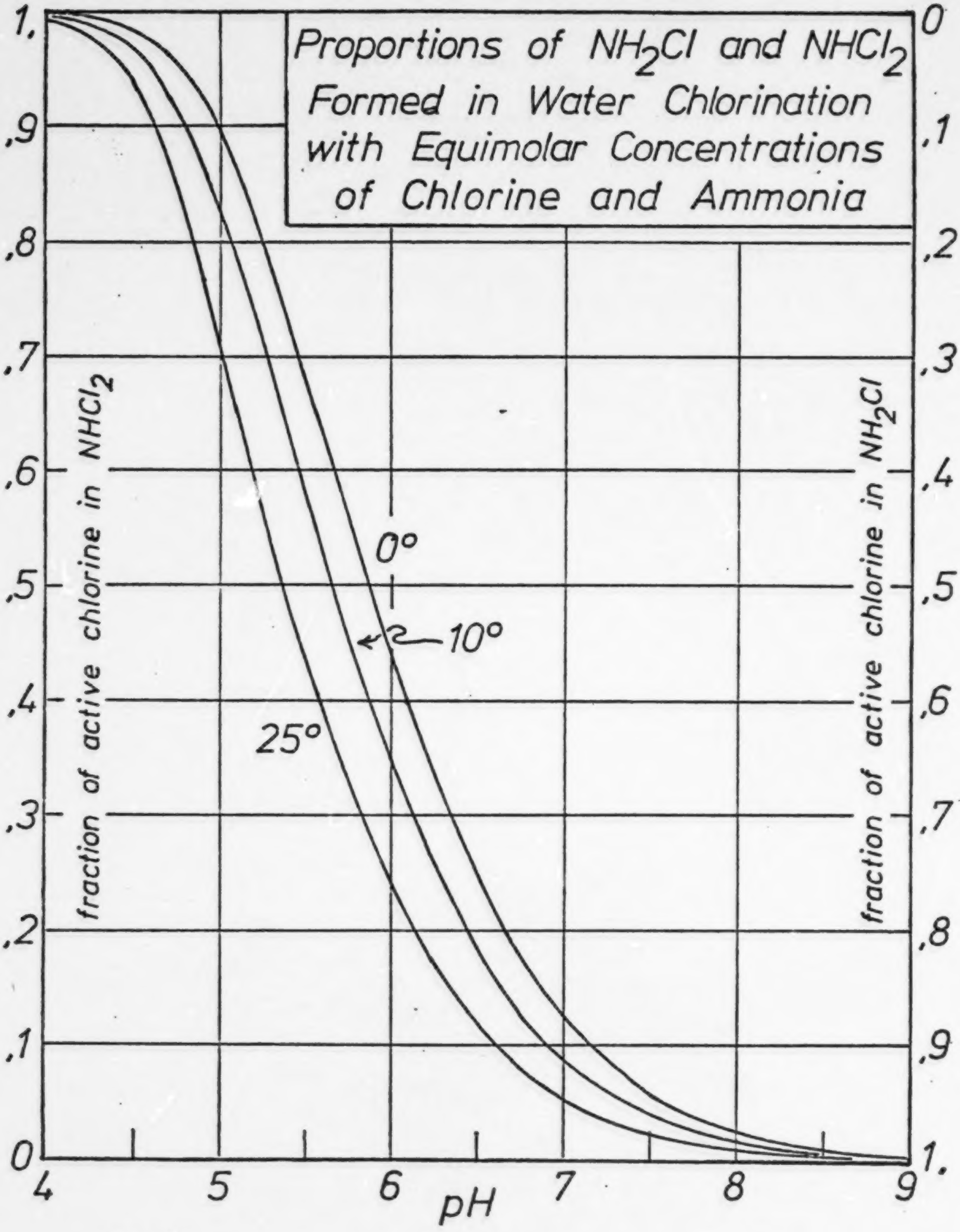


Figure 3 Proportions of NH_2Cl and $NHCl_2$ Formed in Water Chlorination with Equimolar Concentrations of Chlorine and Ammonia

1, monochloramine is formed, thereby creating the "peak" shown in Figure 4. At values greater than 1, dichloramine is formed. Being unstable, it decomposes, usually as indicated in Reaction 7. Thus, with the addition of chlorine the apparent chlorine residual decreases from a chlorine-to-ammonia molar ratio of 1 up to approximately 1.65, at which the breakpoint occurs, i.e., after the ammonia has been converted principally to nitrogen (N_2) and some nitrate (Figure 4). Chlorine that is added after the breakpoint exists as free chlorine, i.e., hypochlorous acid and the hypochlorite ion (OCl^-) (Morris, 1978; Wei, 1972; Wei and Morris, 1974).

Chloramine By-Products Found in Drinking Water and Selected Nonpotable Waters

Very few chemical studies of drinking water have been designed to identify the products resulting from the reaction of chloramines with organic or inorganic constituents of the water supplies.

Monochloramine is less effective as a chlorinating agent than hypochlorous acid by a factor of approximately 10^4 (Morris, 1967). Presumably, many of the reaction products of chlorination of water will be formed from chloramination because of the hydrolysis of chloramines to hypochlorous acid; however, the products should occur in lower concentrations because of the low equilibrium concentrations

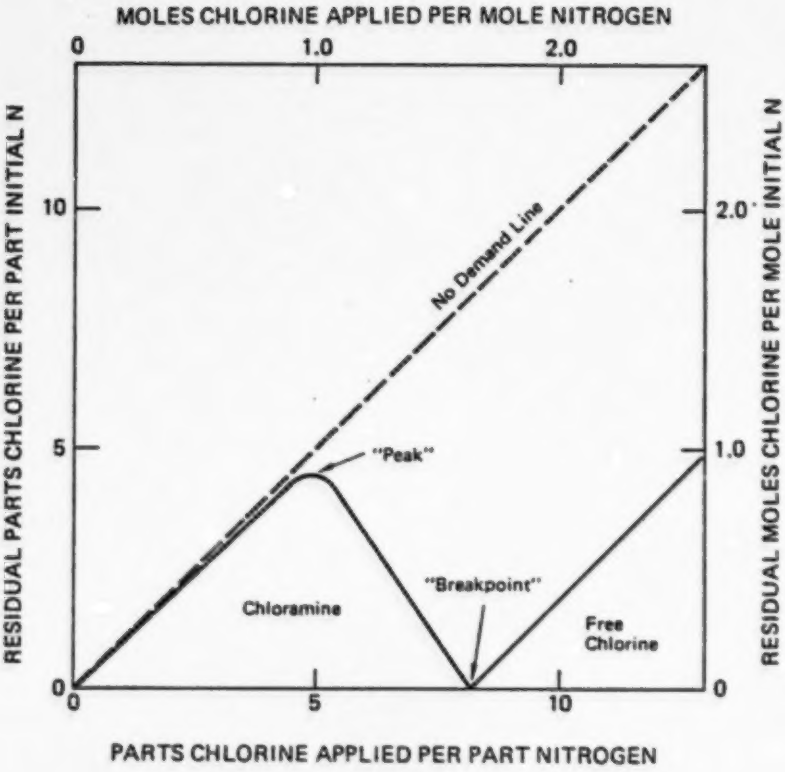


Figure 4 Diagramatic Representations of Completed Breakpoint Reaction. (Breakpoint reactions are significant in the pH range 6 to 9 and are most rapid at pH's 7.0 to 7.5) (From Morris, 1978)

of the acid. According to Margerum and Gray (1978) the hydrolysis of monochloramine:

$$NH_2Cl + H_2O \longrightarrow HOCl + NH_3 \qquad (8)$$

has a reaction half-time of 10 hr. The equilibrium constant is $K = 6.7 \times 10^{-12}$.

Margerum and Gray (1978) indicate that the formation of hydroxylamine (NH_2OH):

$$NH_2Cl + OH^- \longrightarrow NH_2OH + Cl^- \qquad (9)$$

at pH 8 has a reaction half-time of 350 years. Therefore, it probably does not occur in water treatment.

Stevens *et al.* (1978) determined that trihalomethane (THM) formation was minimized when chloramines (mostly monochloramine) were used to treat raw water. Chlorine was added at 5.5 mg/l to raw water and to raw water spiked with 20 mg/l ammonium chloride (NH_4Cl) (ammonia nitrogen, 5.2 mg/l) (See Figure 5). Thus, during chlorination of water where the ammonia breakpoint is not achieved, THM production may not be great (Stevens *et al.*, 1978).

Rickabaugh and Kinman (1978) determined that chloramination of Ohio River water with monochloramine at 10 mg/l, pH 7 to 9, and 25°C resulted in 90.7% to 99.9% less production of THM as compared with THM production from chlorination with 10 mg/l chlorine as hypochlorous and hypochlorite ion.

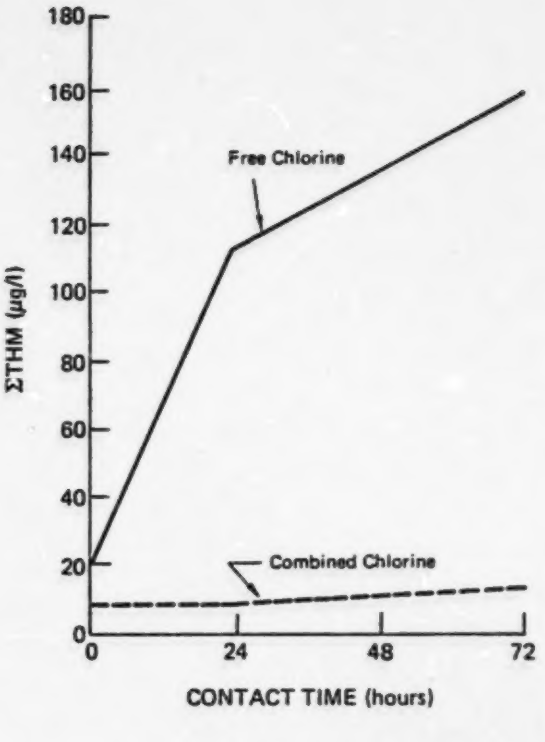


Figure 5 Comparison of THM Formation with Free and Combined Chlorine in Ohio River Water, at pH 7.0 and 25°C. (Chlorine dosage 5.5 mg/l: free chlorine values represent raw water, combined chlorine values represent raw water spiked with 20 mg/l ammonium chloride) (Based on Stevens et al., 1978; Symons et al., 1977).

In the 1975 National Organics Reconnaissance Survey (NORS), 10 of the 80 water supplies sampled had been disinfected with chloramines. The concentration of THM's in the finished water of these utilities ranged from 1 to 81 μg/l with an average of 19 μg/l. The THM concentrations in treatment plants using breakpoint chlorination ranged from 1 to 472 μg/l, averaging 72 μg/l (Symons et al., 1977).

Chloramination of Model Compounds

N-chloroorganic compounds, such as N-chloroglycine [$H(Cl)NCH_2COOH$] and chlorophenols, may be by-products of the chloramine water treatment process.

According to Margerum and Gray (1978), monochloramine is a chlorinating agent for N-compounds in aqueous solutions. For example, with 10^{-4} M glycine the following reaction takes place:

$$NH_2Cl + H_2NCH_2COOH \longrightarrow H(Cl)NCH_2COOH + NH_3 \qquad (10)$$

The rate constant (K) for this reaction is 1.5 $M^{-1}s^{-1}$ at pH 5 to 9, making it or similar reactions probable in aqueous systems. This report also corroborates the observation of Ellis and Soper (1954) that monochloramine undergoes chlorine-exchange reactions with primary and secondary aliphatic amines.

Although initially no chlorophenols are formed when low concentrations (milligram-per-liter range) of monochloramine and phenol are mixed, they appear after a reaction time of several days (Burttschell et al., 1959).

Inferences of Possible Chloramine Reaction By-Products

Reaction products from aqueous chloramine reactions are presented in Table 5. The types of reaction are quite varied. They include addition, chlorine substitution, oxidation, amination, and free radical reactions. The majority of these reactions involve either highly acidic or highly alkaline solutions. Thus, deducing or inferring the presence of such reaction by-products in the chloramine water treatment process is a highly speculative activity. This is particularly true if the substrate is present in the water supply only in trace or very low concentrations. Much of the considerable reported research concerning chloramine reactions used organic solvents, such as ether. Because reactions in organic solvents have limited value in predicting by-products of the chloramine water treatment process, they were not included in Table 5.

Reactions of chloramides, such as chloramine-T ($p\text{-}CH_3C_6H_4SO_2NCl^-Na^+$) have been studied extensively. Selected recent papers have been referenced in Table 6. If present at all, such chloramides would occur in the water treatment process only at very low concentrations. However, similar reaction products would be anticipated from chloramine reactions. The reaction summaries in Table 6 include several substrates, e.g., carbohydrates that might be present in water supplies. They indicate that reaction by-products such as aldonic acids could occur in the chloramine water treatment process.

TABLE 5 Aqueous Chloramine Reactions with Organic Compounds: Summary of Reaction Products

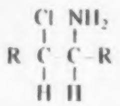
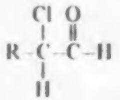
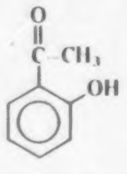
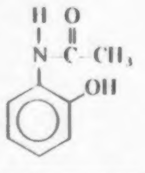
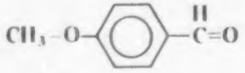
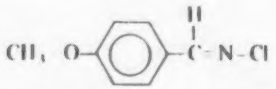
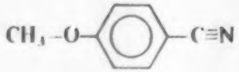
Substrate	Products	Reaction Conditions	Reference
Olefins $R-CH=CH-R' + NH_2Cl$	β-chloramines  $R-\overset{\overset{Cl}{\vert}}{\underset{\underset{H}{\vert}}{C}}-\overset{\overset{NH_2}{\vert}}{\underset{\underset{H}{\vert}}{C}}-R$	0.5 M chloramine, 4 M H_2SO_4, 20°C	Neale, 1964
Acetylenes $R-C\equiv C-H + NH_2Cl$	β-chloroaldehydes  $R-\overset{\overset{Cl}{\vert}}{\underset{\underset{H}{\vert}}{C}}-\overset{\overset{O}{\Vert}}{C}-H$	0.5 M chloramine, 4 M H_2SO_4, 20°C	Neale, 1964
o-Hydroxyacetophenone 	2-Acetamidophenol 	0.5 M monochloramine, pH ∼ 13, 0°C	Crochet *et al.*, 1973
Anisaldehyde 	Anisalchlorimine  Anisonitrile 	Monochloramine, 0°C	Hauser and Hauser, 1930

TABLE 5 (continued)

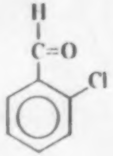
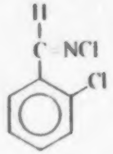
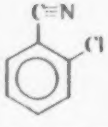
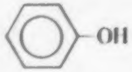
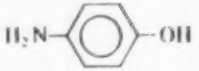
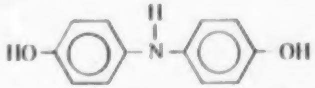
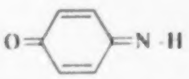
o-Chlorobenzaldehyde 	o-Chlorobenzalchlorimine  o-Chlorobenzonitrile 	Monochloramine, 0°C	Hauser and Hauser, 1930
Formaldehyde H_2CO	N-trichlorotrimethyl-enetriamine $(CH_2NCl)_3$	0.5 M monochloramine, 15°C	Cross *et al.*, 1910; Lindsay and Soper, 1946
Phenol[a] 	p-Aminophenol  4,4'-Dihydroxydiphenylamine  Iminoquinone  and also quinone chlorimide and indophenol blue.	Monochloramine, neutral pH	Raschig, 1907; Harwood and Kuhn, 1970; Standard Methods, 1975

TABLE 5 (continued)

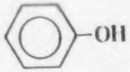
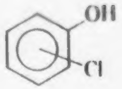
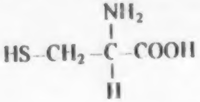
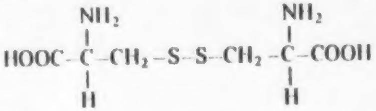
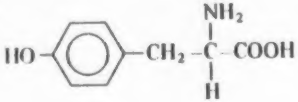
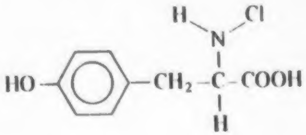
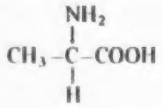
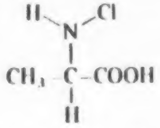
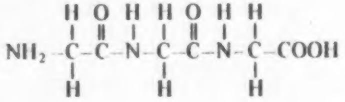
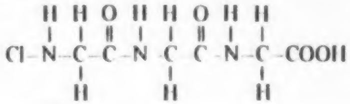
Substrate	Products	Reaction Conditions	Reference
Phenol 	Chlorophenols 	Monochloramine at ppm conc., Several days	Burtschell *et al.*, 1959
Thiol groups R–SH	Sulfides R–S–S–R	Monochloramine and dichloramine	Srivastava and Bose, 1975
Thiols R–SH	Sulfenamides $R-S-NH_2$	Monochloramine, pH 12	Sisler *et al.*, 1970
Cysteine  $HS-CH_2-\underset{H}{\overset{NH_2}{C}}-COOH$	Cystine  $HOOC-\underset{H}{\overset{NH_2}{C}}-CH_2-S-S-CH_2-\underset{H}{\overset{NH_2}{C}}-COOH$	Monochloramine 0.5-1.5 ppm, pH 8	Ingols *et al.*, 1953
Tyrosine 	N-Chlorotyrosine 	Monochloramine 0.5-1.5 ppm, pH 8	Ingols *et al.*, 1953

TABLE 5 (continued)

Alanine  $CH_3-C(NH_2)(H)-COOH$	N-Chloroalanine  $CH_3-C(NHCl)(H)-COOH$	Monochloramine 0.5-1.5 ppm, pH 8	Ingols *et al.*, 1953
Glycylglycylglycine  $NH_2-CH_2-CO-NH-CH_2-CO-NH-CH_2-COOH$	Terminal N-chloro-compound, N-chloroglycylglycylglycine  $Cl-NH-CH_2-CO-NH-CH_2-CO-NH-CH_2-COOH$	Monochloramine 0.5-1.5 ppm, pH 8	Ingols *et al.*, 1953
DNA	Unidentified	Monochloramine	Shih and Lederberg, 1976a, 1976b
Iodide	Iodine and hypoiodous acid	Monochloramine	Kinman and Layton, 1976; Standard Methods, 1975
Activated carbon	N_2 and NO_3^-, Organics unidentified	Monochloramine, pH 7.4 Dichloramine, pH 7.4	Bauer and Snoeyink, 1973; Stasiuk, 1974

[a] This reaction may be time dependent and may not occur with preformed monochloramine.

TABLE 6 Aqeous Chloramide Reactions with Organic Compounds: Summary of Reaction Products

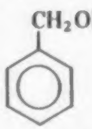
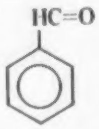
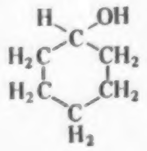
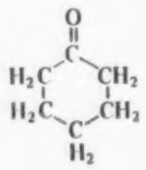
Substrate	Products	Reaction Conditions	Reference
Allyl alcohol $CH_2{=}CH{-}CH_2OH$	Acrolein $CH_2{=}CH{-}CHO$	Chloramine-T, pH ∼ 1	Mahadevappa and Naidu, 1973
Benzyl alcohol 	Benzaldehyde 	0.02 M Chloramine-T, pH 1-2, acetic acid and perchloric acid, 25°C	Banerji, 1977
n-Butanol $CH_3CH_2CH_2CH_2OH$	n-Butanal $CH_3CH_2CH_2CHO$	Chloramine-T, pH 4-5.5, 45-60°C	Mushran *et al.*, 1974
Iso-butanol $(CH_3)_2CHCH_2OH$	Iso-butanal $(CH_3)_2CHCHO$	Chloramine-T, pH 4-5.5, 45-60°C	Mushran *et al.*, 1974
Iso-pentanol $(CH_3)_2CH_2CH_2CH_2OH$	Iso-pentanal $(CH_3)_2CH_2CH_2CHO$	Chloramine-T, pH 4-5.5, 45-60°C	Mushran *et al.*, 1974
Crotyl alcohol $CH_3CH{=}CHCH_2OH$	Crotyl aldehyde $CH_3CH{=}CHCHO$	0.1 N Chloramine-T, pH 1-7, 25°C	Naidu and Mahadevappa, 1976
Cyclohexanol 	Cyclohexanone 	Chloramine-T, pH 5, 50°C	Kumar *et al.*, 1976

TABLE 6 (continued)

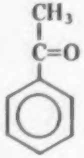
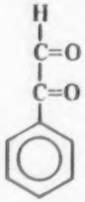
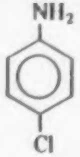
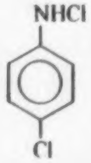
Propan-2-ol $CH_3CH(OH)CH_3$	Not identified	Chloramine-T, pH ∿ 1	Natarajan and Thiagarajan, 1975
Xylose, arabinose, Mannose, galactose	Aldonic acids	Chloramine-T, highly alkaline, 45°C	Agrawal and Mushran, 1973
D(–)Ribose	Aldonic acid	Chloramine-T, pH ∿ 13, 32.5°C	Mushran *et al.*, 1974
D(+)Sorbose	Xylonic acid, Formaldehyde	0.002 M Chloramine-T, pH ∿ 13, 50°C	Sanehi *et al.*, 1975
Hydroquinone, hydrazine, cinnamic acid, and ascorbic acid	Not identified	Dichloramine-T	Nair and Nair, 1973
Acetophenone 	Phenyl glyoxal 	Chloramine-T, ethanol, pH ∿ 13, 55°C	Kumar *et al.*, 1975
p-Chloro-, p-bromo-, and p-nitroanilines e.g. 	Substituted N-Chloroanilines e.g. 	Chloramine-T, pH 7.4, 50°C	Trieff and Ramanujam, 1977

TABLE 6 (continued)

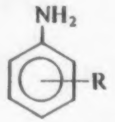
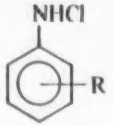
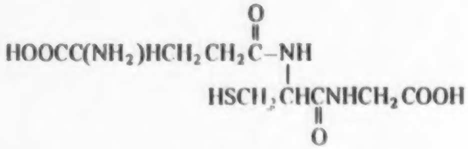
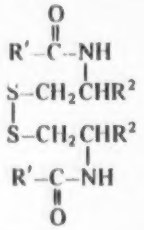
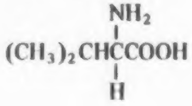
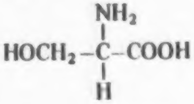
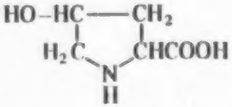
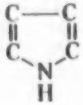
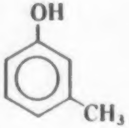
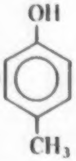
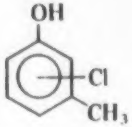
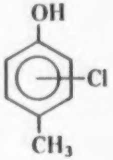
Substrate	Products	Reaction Conditions	Reference
Aniline and substituted anilines 	N-chloroanilines 	Chloramine-T, 50% ethanol, pH 7.4, 25-20°C	Ramanujam and Trieff, 1977
Glutathione  $\mathrm{HOOCC(NH_2)HCH_2CH_2\overset{O}{\overset{\|}{C}}-NH}$ $\mathrm{HSCH_2CH\underset{\underset{O}{\|}}{C}NHCH_2COOH}$	Glutathione disulfide  $\mathrm{R'-\overset{O}{\overset{\|}{C}}-NH}$ $\mathrm{S-CH_2CHR^2}$ $\mathrm{S-CH_2CHR^2}$ $\mathrm{R'-\underset{\underset{O}{\|}}{C}-NH}$	0.1 N Chloramine-T, pH 1.4 or 0.N Dichloramine-T, 25°C	Mahadevappa and Gowda, 1975
Thiols (e.g., cysteine) See Table 5.	Disulfides (e.g., cystine) See Table 5.	Chloramine-T, pH ∼ 1	Gowda *et al.*, 1975
Valine, leucine, and phenylalanine e.g., valine  $\mathrm{(CH_3)_2CH\overset{NH_2}{\overset{\|}{\underset{\underset{H}{\|}}{C}}}COOH}$	Nitriles e.g., 3 methylproprionitrite $\mathrm{(CH_3)_2CHCN}$	0.1 N Chloramine-T, pH 5	Mahadevappa and Naidu, 1976

TABLE 6 (continued)

Phenylalanine and serine e.g., Serine  $HOCH_2-\underset{H}{\overset{NH_2}{C}}-COOH$	Nitriles e.g., hydroxyacetonitrite $HOCH_2CN$	Chloramine-T, pH 11-12, 40-45°C	Kumar *et al.*, 1976
Hydroxyproline 	Pyrrole 	Chloramine-T	Mani and Radhakrishnan, 1976
m- or p-Cresol (m-)  or (p-) 	Chlorinated cresol  or 	Chloramine-T, pH 1-10, max. rate pH 4.5	Antelo *et al.*, 1974

BROMINE AND IODINE

The use of chlorine for disinfection of public water supplies has proved so successful that there has been little impetus to test alternative halogens. In the late 1930's, bromine was used briefly at Irvington, California, but was abandoned because it was difficult to handle, it produced undesirable tastes, and a residual could not be maintained in the distribution system (White, 1972, p. 712). During the 1920's, iodine was added to the water supplies at Rochester, New York, and Sault Sainte Marie, Michigan. One reason for its use in these cases was goiter prevention, but this motivation disappeared with the advent of iodized table salt (Laubusch, 1971). A long-term study of physiological effects of iodinated drinking water was conducted in Florida prisons (Black *et al*., 1968; Breund *et al*., 1966).

Both bromine and iodine have been used in swimming pool disinfection. In addition, iodine that is administered in Globaline tablets whose active ingredient is tetraglycine hydroperiodide, $2[(NH_2CH_2COOH)_4HI] \cdot 2\ 1/2\ I_2$, has been adopted by the military to disinfect individual water supplies. Unfortunately, none of these applications has provided data on trace by-products. Therefore, an assessment of the potential of bromine and iodine to produce hazardous substances at the trace level must be based on less direct evidence.

Properties of Bromine and Iodine

Bromine and iodine may be introduced into water in several ways: in pure elemental form (Br_2 liquid or I_2 solid), as interhalogen compounds such as bromine chloride (BrCl) (Mills, 1975), or they may be released from various organic substrates (Goodenough et al., 1969; Morris et al., 1953). They may also be generated within the water by oxidizing bromide or iodide with an agent such as chlorine. Once the halogen has been introduced into water, it reacts rapidly. Consequently, its ultimate chemical form is controlled mainly by the composition and temperature of the water rather than by the nature of the halogen source.

Various aspects of bromine chemistry have been discussed recently by Johnson and Overby (1971), LaPointe et al. (1975), and Sugam (1977). In pure water containing no amino-nitrogen, the predominant form of bromine at near-neutral pH is hypobromous acid (HOBr). Above pH 8.6 at 25°C, this gives way to the hypobromite ion (OBr^-). At pH values below 6, hypobromous acid will convert to Br_2, Br_3^-, bromine chloride, or other halide complexes. The exact nature of the predominant species and the exact pH of the transition is controlled by the halide composition of the water (Sugam, 1977). However, at the pH and halide levels of drinking waters, halide complexes are not abundant. In the presence of ammonia or organic amines, bromamines are formed. Unlike the analogous chloramines, the inorganic bromamines are labile and interconvert rapidly so that the species distribution is controlled by chemical equilibrium (Johnson and Overby, 1971). The bromoamines decompose readily into primarily nitrogen gas and bromide (LaPointe et al., 1975). At temperatures above approximately 70°C, alkaline hypobromite solutions decompose rapidly to yield the thermodynamically more stable anions bromate (BrO_3^-) and bromide (Br^-). At ordinary temperatures and at near-neutral pH this reaction is very slow (Engel et al., 1954); however, Macalady et al. (1977) have shown that the rate is appreciable in seawater under bright sunlight.

Iodine chemistry in drinking water has been discussed in detail by Chang (1958). Iodine differs from chlorine and bromine in several notable ways. Iodoamines are unstable and do not form to any appreciable extent in aqueous solutions. Hypoiodite (OI^-), which becomes a predominant species only at very high pH, is not of practical importance because of the tendency of hypoiodous acid (HOI) to decompose rapidly to iodate (IO_3^-) plus iodide (I^-) above pH 9.

$$3OH^- + 3HOI \text{ -----> } IO_3^- + 2I^- + 3H_2) \qquad (11)$$

This decomposition is much faster than the analogous bromine reaction and results in a loss of most of the disinfecting capacity of the iodine. Unlike oxyanions of chlorine and bromine, iodate is thermodynamically stable in oxygenated water. Once formed, it is likely to be persistent. Also in contrast to both bromine and chlorine, the diatomic form of iodine (I_2) is fairly stable in aqueous solutions and can be the predominant species in neutral to acidic solutions. The exact pH at which hypoidous acid predominance gives way to iodine depends upon the iodide concentration. If iodide is greater than approximately 10^{-3}M, then iodine is replaced by I_3^- as the predominant species in neutral to acidic solutions.

Although the predominant chemical form of a halogen under specified conditions of dose, pH, ionic strength of the halide concentration, and temperature can usually be predicted precisely, it may not be the active chemical species in disinfection or in the formation of organic byproducts. The long-standing debate over the role of transient species, e.g., Cl^+, Br^+, H_2OBr^+, H_2OI^+, etc., in aromatic substitution reactions (Berliner, 1966; Gilow and Ridd, 1973; Swain and Crist, 1972) illustrates the difficulties, and, commonly, the ambiguities that are associated with attempts to identify the active species.

With respect to their persistence in distribution systems, alkyl bromides and iodides are somewhat more labile than alkyl chlorides. The data in Table 7 indicate that carbon-bromine and carbon-iodine bonds are somewhat weaker than carbon-chlorine bonds and are considerably weaker than the carbon-fluoride bond. The relative hydrolysis rates for methyl bromide (CH_3Br) and methyl iodide (CH_3I) are correspondingly greater than for methyl chloride (CH_3Cl) and

TABLE 7

Comparison of Bond Energies and Relative Hydrolysis Rates for Methyl Halides

Carbon-Halogen	Bond Energy[1] kcal/mle	Relative Hydrolysis Rate[2]
Methyl fluoride	105.4	0.04
Methyl chloride	78.5	1
Methyl bromide	65.9	28
Methyl iodide	57.4	16

[1] Pauling, 1960

[2] Moelwyn-Hughes, 1971

methyl fluoride (CH_3F). Actual hydrolysis rates for trihalomethanes (THM's) and other disinfection by-products in distribution systems have not yet been determined. Although the bromo and iodo compounds hydrolyze relatively faster than the chloro compounds, absolute rates may be too slow for these reactions to have practical significance.

Bromine and Iodine By-Products Found in Drinking Water or Selected Nonpotable Waters

Experience with Drinking Water Supplies

Since neither bromine nor iodine are used to disinfect major public water supplies, it is only possible to establish the tendency of these disinfectants to produce hazardous by-products in the laboratory. However, it is possible to gain some insight into the problem by examining data for chlorinated water supplies. In these, traces of bromine and iodine are commonly produced by oxidation of very small amounts of bromide and iodide in the raw water. This phenomenon was first reported by Rook (1974) who discovered chloroform ($CHCl_3$), bromodichloromethane ($CHCl_2Br$), dibromochloromethane ($CHClBr_2$) and bromoform ($CHBr_3$) in chlorinated drinking water in Rotterdam. He showed that the ratio of ΣBr to ΣCl in the THM's was in excess of the Br(I) to Cl(I) ratio in the water even if quantitative oxidation of the trace bromide was assumed.

This indicated that the THM formation kinetics favored bromine selectively.

Rook's observations have been confirmed in many water treatment systems throughout the world. Abundant documentation substantiates that THM's are produced mostly by the chlorination process and are quite rare in the raw water (e.g., see Bellar _et al_., 1974; Henderson _et al_., 1976; Environmental Health Directorate, Canada, 1977). In addition to the four bromo-chloro haloforms, dichloroiodomethane ($CHCl_2I$) is sometimes observed. In the National Organic Monitoring Survey (NOMS) of the Environmental Protection Agency, this compound was found in 85 of 111 supplies during Phase II of the survey and in 50 of 105 supplies during Phase III, but it was not quantified. Iodine-containing THM's are probably underrepresented in the data on water supplies because the isolation techniques that are used in analysis are usually not very suitable for these relatively nonvolatile compounds. Nevertheless, the total organically bound iodine that can be produced by chlorinating drinking waters will be severely limited by the iodide in the raw water. Typical iodide concentrations in river waters are below 10 μg/l (Livingstone, 1963; Turekian, 1971).

Shackelford and Keith (1976) listed 20 organic compounds containing bromine and iodine and the number of reports of their presence in water supplies (Table 8). These compounds were not necessarily produced by disinfection. Indeed, this

TABLE 8

Organobromides and Iodides Reported to be Found in Finished Drinking Water.[1]

Parent Compound, Derivative	Parent Compound, Derivative
Acetylene, bromo	Methane, bromochloro
Benzene, bromo	Methane, bromochloroiodo
Benzene, bromochloro	Methane, bromodichloro
Benzene, dibromo	Methane, chlorodibromo
Butane, bromo	Methane, dibromo
Butane, dibromochloro	Methane, dibromodichloro
Butane, dibromodichloro	Methane, dichloroiodo
Ether, bromophenyl, phenyl	Methane, iodo
Ethylene, bromotrichloro	Methane, tribromo
Methane, bromo	Propane, 2 bromomethyl

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[1] Data from Shackelford and Keith, 1976.

would be unlikely in many cases. However, the list is very instructive because of the clear analytical bias that it displays. All of the compounds are nonpolar, and most have relatively low molecular weight and high volatility. Undoubtedly, many compounds are overlooked because of limitations in the analytical methods that are used most frequently. For example, in view of the ease with which they form, it is surprising that there have been no reports of bromophenols in drinking water. The NOMS study produced evidence that 2,4-dichlorophenol ($C_6H_3(Cl)_2OH$) is produced by chlorination of drinking waters. It seems likely that some bromophenols would also have been produced, but this remains to be established.

These studies of chlorinated water supplies show that large amounts of THM's would probably result if bromine or iodine replaced chlorine as the principal disinfectant since THM's containing bromine and iodine are produced from traces of oxidized bromine and iodine.

Laboratory Studies with Potable Waters

The conclusion in the previous paragraph is also supported by several laboratory studies of river waters. Bunn *et al*. (1975) treated Missouri River water both with chlorine, in the form of calcium hypochlorite [$Ca(OCl)_2$], and with mixtures of chlorine and halide salts. This is analogous to the treatment of some swimming pools to which bromide or iodide salts are added and then oxidized with chlorine. The results of Bunn et al. reveal that the addition of potassium fluoride (KF) or potassium chloride (KCl) has little effect on the composition of the THM products (Table 9). But in the presence of potassium bromide (KBr) or potassium iodide (KI), appreciable amounts of these halogens are incorporated into the THM products.

Similar experiments were performed by Rickabaugh (1977) and Rickabaugh and Kinman (1978). They treated Ohio River waters with hypochlorous acid (HOCl), hypochlorous acid plus iodide, monochloramine (NH_2Cl), monochloramine plus iodide, and iodine at pH's between 7.5 and 9.0. In addition to the usual four chlorine- and bromine-containing THM's, they found dichloroiodomethane and bromochloroiodomethane (CHBrClI) when iodine was present. On a molar basis, the total yield of THM's increased with pH. Ten mg/l of iodine produced 5 to 10 times less total THM than 10 mg/l of hypochlorous acid. Treatment with monochloramine or monochloramine plus iodide produced even smaller amounts. It would be unwise to generalize too much from these data since the doses were not comparable on a molar basis. Moreover, little is known about the relative halogen demands under the different treatment conditions. Nevertheless, they suggest that iodine may be a less potent generator of THM's than chlorine.

TABLE 9

Effect of Added Potassium Halide on THM Formation in Missouri River Water[1]

Halide Added	THM's, µ/l Chloroform	Bromodichloromethane	Dibromochloromethane	Bromoform
None	172	20	1	<1
1 ppm fluoride	158	17	1	<1
1 ppm chloride	166	18	1	<1
1 ppm bromide	21	35	30	50
1 ppm iodide[2]	67	15	1	<1

[1] Data from Bunn *et al.*, 1975. Dose: 7 ppm chlorine from calcium hypochlorite.

[2] Substantial amounts of dichloroiodomethane, chlorodiiodomethane ($CHClI_2$), and triiodomethane (CHI_3) were found but not quantified.

Experience with Nonpotable Waters

Kuehl *et al*. (1978) studied brominated organic compounds in the tissues of fathead minnows that had been exposed to sewage effluent treated with bromine chloride. The compounds that they found and their estimated concentrations are given in Table 10. These compounds were identified by mass spectrometry. None of the compounds were found in control fish, which were exposed to effluent that had not been treated with bromine chloride. An obvious interpretation is that these compounds were synthesized by reaction of the bromine chloride with organic compounds in the effluent. The authors caution that they cannot rule out the possibility that the enhanced bromide levels in the exposed fish caused biosynthesis of brominated compounds. Unfortunately, the effluent water was not analyzed.

Bean *et al*. (1978) examined the compounds that were recovered from XAD-2 resin through which chlorinated seawater had been passed. The bromide content of untreated seawater is about 65 mg/l, well in excess of chlorine doses that are typically used for disinfection. Thus, in chlorinated seawater, bromide oxidizes rapidly, forming mainly brominated organic by-products (Helz and Hsu, 1978). Using gas chromatography and mass spectrometry, Bean *et al*. found several halogenated compounds including bromoform, bromoacetal [$BrCH_2CH(OC_2H_5)_2$], and various brominated aromatic compounds. Since the seawater was not

TABLE 10

Brominated Compounds in Fish Exposed to Secondary Effluent Treated with Bromine Chloride at Grandville, Michigan.[1]

Compound	Estimated Concentration, ng/g
Bromoindole[2]	100-200
Dibromoindole[2]	10-50
Tribromoindole	10-50
Tetrabromoindole	10-50
Dibromomethylindole[2]	10-50
Tribromomethylindole	10-50
Tetrabromomethylindole	10-50
Dibromomethylbenzthiazole	5-25
Dibromophenol	10-50
Tribromophenol[2]	50-100
Chlorodibromophenol	5-25
Dichlorobromophenol	5-25
Dibromomethylphenol	5-25
Dibromoanisole	10-50
Tribromoanisole[2]	50-100

[1] Data from Kuehl *et al*. (1978)

[2] Compounds also found in fish at the treatment plant in Wyoming, Michigan.

dechlorinated prior to its passage through the resin, it is not clear which compounds were formed in the seawater and which were formed in the resin by reaction with bromine in the seawater. The authors concluded that, except for bromoform, the concentration of nonpolar halogenated compounds that were generated by chlorination of relatively pristine seawater appears to be very low, i.e., in the nanogram per liter range.

Bromination of Model Compounds

Rook _et_ _al_. (1978) reported a series of experiments in which they compared the reactivity of chlorine and bromine to peat extracts and to several hydroxybenzene and methoxybenzene model compounds. When these two halogens were applied to peat extracts at the same molar level, the bromine tests produced about twice the molar yield of THM's in a 4-hour period. This was coupled with a much faster oxidant decay rate in the bromine tests. Experiments with the model compounds showed that both oxidants were more reactive at high pH. Chlorine reacted readily with both 1,3-dihydroxybenzene [$C_6H_4(OH)_2$] and 1,3-dimethoxybenzene [$C_6H_4(CH_3O)_2$]. There was very little chlorine substitution with the 1,3-dimethoxybenzene since the reaction was mainly oxidative. In contrast, there was efficient substitution in both organic substrates when bromine was used. Since organic matter in natural waters is believed to include material containing hydroxybenzene and methoxybenzene structures, these experiments support the notion that bromine may be more effective than chlorine in generating haloorganic compounds.

Discussion and Conclusions

The unsatisfactory state of knowledge concerning potentially hazardous substances that might be generated in drinking water through disinfection with bromine or iodine results from the absence of data from operational water treatment systems. However, the evidence suggests that the behavior of these halogens will be qualitatively similar to chlorine. At the very least, the production of THM's can be anticipated. Traces of halogenated phenols and nitrogen heterocycles also seem likely. Some tenuous evidence suggests that the total THM yield would be greater for bromine than for chlorine, but less for iodine than for chlorine. Factors such as cost, adequacy of supply, adverse physiological effects of constant exposure to iodide and its disinfectant efficacy are pertinent concerns when considering iodine as a replacement for chlorine in public water supply disinfection.

CHLORINE DIOXIDE

Chlorine dioxide (ClO_2) is an orange-yellow gas with a liquefaction temperature of 9.7°C at atmospheric pressure. It is explosive in either its gaseous or pure liquid state (Robson, 1964). Accordingly, it is usually prepared in solution at the place and time of use.

Properties of Aqueous Chlorine Dioxide

According to Henry's law the coefficient for aqueous solubility of chlorine dioxide is 1.0 moles/l/atm. at 25°C and 3.1 moles at 0°C (Gordon et al., 1972). Dilute gas mixtures with less than 0.1 atm. partial pressure of chlorine dioxide and dilute aqueous solutions are not explosive; they may be handled with ordinary precautions. However, even dilute aqueous solutions are somewhat unstable, particularly in light, tending to decompose through reactions that will be described later. Fresh solutions must be prepared daily and must be protected from light to be suitable as reproducible stock or test solutions.

Two principal methods are used for the preparation of aqueous solutions of chlorine dioxide for water treatment (Gall, 1978; Masschelein, 1967, 1969). The first, which is used in the United States almost exclusively, is the reaction of sodium chlorite ($NaClO_2$) and chlorine (Cl_2) in acidic aqueous solution, primarily by the following equation:

$$HOCl + 2\ ClO_2^- + H^+ = 2\ ClO_2 + Cl^- + H_2O$$

Reaction 12 is not entirely stoichiometric. Side reactions producing chlorate (ClO_3^-) consume some extra chlorine, so that an excess over the proportion that is indicated by the equation is required to utilize the chlorite (ClO_2^-) fully. For stoichiometric reaction, according to Reaction 12, 0.39 part of chlorine as Cl_2 is required for each part of sodium chlorite. In practice 0.5 to 1.0 part of chlorine per part of technical sodium chlorite (80%) is commonly used (Dowling, 1974; Gall , 1978; Symons _et al_., 1977). The solution resulting after completion of Reaction 12 then contains excess aqueous chlorine and some chlorate along with the chlorine dioxide.

According to Masschelein (1969), optimal yields of chlorine dioxide, (90% to 95% of the theoretical yield based on sodium chlorite), are obtained by mixing a strong sodium chlorite solution (300 g/l) with aqueous chlorine solution containing 2 to 3 g/l of Cl_2. The mixed solution is then usually passed through a reactor that is packed with inert turbulence-promoting material to give a contact time of 1 to several minutes for reaction. The resulting solution, containing 3 to 5 g/l of chlorine dioxide, may be dosed directly into the water being treated or may be diluted to about 1 g/l for short-term intermediate storage before dosing. The other method of preparing chlorine dioxide for use in water treatment is acidification of strong sodium chlorite solution, usually with hydrochloric acid (HCl). The major reaction is

$$5\ ClO_2^- + 4\ H^+ = 4\ ClO_2 + Cl^- + 2\ H_2O \qquad (13)$$

Side reactions leading to the formation of chlorate and even elemental chlorine also occur in this system, as in the other (Gordon et al, 1972; Taylor, et al., 1940). The side reactions are minimized when hydrochloric acid is used at a 1 to 2 molar concentration and mixed in excess with a strong sodium chlorite solution (Beuerman, 1965; Kieffer and Gordon, 1968; Masschelein, 1969; Toussaint, 1972).

According to Reaction 13, 0.322 part of hydrochloric acid is required per part of sodium chlorite for stoichiometric reaction. In practice, approximately equal parts, representing a three-fold excess of hydorchloric acid, have been used. After a few minutes of contact to allow reaction to proceed to completion, the concentrated mixture may be dosed directly or given intermediate storage as in the previous method.

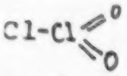
The latter method, sometimes with an acid other than hydrochloric acid, has often been preferred for laboratory preparation of chlorine dioxide solutions as a means of avoiding the presence of excess aqueous chlorine (Dowling, 1974; Granstrom and Lee, 1957, 1958). Since chlorine or hypochlorous acid (HOCl) may be a product of decomposition of chlorous acid ($HClO_2$) under some conditions; however, the method does not assure freedom from contamination by aqueous chlorine unless special precationary techniques are followed (Feuss, 1964; Miltner, 1977). Failure to observe such precautions casts doubts on a number of reported findings of chlorinated products from the reaction of aqueous chlorine dioxide with organic matter. For industrial use, especially in the pulp and paper industry where much greater amounts are used than in water treatment, chlorine dioxide is prepared by reduction of sodium chlorate ($NaClO_3$) with agents such as sulfur dioxide (SO_2), methanol (CH_3OH), or chloride (Cl^-), generally in several molar sulfuric acid (H_2SO_4) solution (Gall, 1978; Sussman and Rauh, 1978). These processes are more economical than those based on sodium chlorite for the manufacture of large quantities of chlorine dioxide. However, they are more complex in operation, the formed chlorine dioxide must be swept from the reaction mixture with a gas stream and redissolved in water, contamination with chlorine usually occurs, and disposal of by-product wastes can be a problem. Nonetheless, adaptation of some of these processes to conditions of water treatment is being attempted (Gall, 1978), and practical methods may develop if demand for chlorine dioxide disinfection increases sufficiently.

The principal side reactions occurring during the preparation of chlorine dioxide solutions are:

$$4HClO_2 \rightarrow 2\ ClO_2 + ClO_3^- + Cl^- + 2\ H^+ + H_2O$$

and

$$HClO_2 + HOCl \rightarrow 2\ H^+ + ClO_3^- + Cl^-$$

These lead, as can be seen, to the formation of chlorate as a significant by-product. Accordingly, the health effects of chlorate must be considered in connection with the treatment of water with chlorine dioxide. Gordon et al. (1972) have discussed these and other reactions that may occur in solutions containing chlorine dioxide, chlorite, and aqueous chlorine. They pointed out that many of the observed reactions appear to proceed through a transitory, common intermediate, Cl_2O_2, with a suggested structure, . This intermediate, may undergo several reactions, including the following:

$$2\ Cl_2O_2 \dashrightarrow Cl_2 + 2\ ClO_2 \qquad (16)$$

This reaction is invoked to account for the appearance of aqueous chlorine in the acid solutions of chlorine dioxide that are used to bleach pulp (Lindgren and Ericsson, 1969; Lindgren and Nilsson, 1972). It may also account for the reported presence of hypochlorous acid or chlorine in reaction mixtures that are used for the preparation of supposedly "chlorine-free" chlorine dioxide (Kieffer and Gordon, 1968; Rosenblatt, 1975, 1978). On the other hand, many of these reports may simply reflect the inadequacy of most analytical methods for discriminating accurately between chlorine dioxide and free aqueous chlorine. Gordon et al. (1972) concluded that the reactions of chlorite plus acid do give chlorine dioxide solutions that are free of chlorine. Chlorine dioxide is reasonably stable in neutral or mildly acid aqueous solutions at concentrations of several milligrams per liter or less provided the solutions are shielded from light (Bowen and Cheung, 1932; Gordon et al., 1972). However, in alkaline solutions, it disproportionates according to the reaction:

$$2\,ClO_2 + 2\,OH^- \longrightarrow H_2O + ClO_2^- + ClO_3^-$$

whose rate has been measured extensively (Gordon, 1964). Another decomposition reaction is:

$$6\,ClO_2 + 3\,H_2O \longrightarrow 6\,H^+ + 5\,ClO_3^- + Cl^-$$

occurs with measurable speed only in quite acid solution (Bray, 1906). As noted earlier, photochemical breakdown takes place readily. The initial reaction appears to be:

$$ClO_2 \xrightarrow{h\nu} ClO + O \qquad (19)$$

but the complete mechanism of the photochemical reaction in solution is unknown. Hydrogen peroxide (H_2O_2), chlorite, chlorate, Cl_2O_3, oxygen (O_2), and chlorine have all been reported as intermediates or products (Gordon et al., 1972). Presumably, the chlorine dioxide will not persist in open basins or reservoirs, although it can remain for days in clean distribution systems. Residual persistence is discussed more fully in another report--The Disinfection of Drinking Water--under preparation by the Safe Drinking Water Committee.

Chlorine dioxide is a strong oxidizing agent. The normal pathway of action in mildly acid, neutral, and alkaline solutions is:

$$ClO_2\,(aq) + e^- \longrightarrow ClO_2^- \qquad (20)$$

for which the standard potential is $E^0 = 0.954$ volts at 25°C. Reduction to chloride also occurs, but only in acid solutions, so that the reaction is of little interest for the usual conditions of water treatment.

Inorganic Reactants.

Iodide (I^-), arsenite (AsO_3^-), and bisulfite (HSO_3^-) are some of the inorganic reductants that are oxidized by chlorine dioxide between pH 5 and 9. The chlorine dioxide is reduced to chlorite (Reaction 19). Manganous ions are also oxidized readily to manganic hydroxides, a reaction that is often used to precipitate manganese as hydroxide in water treatment (Sussman and Rauh, 1978; Symons _et al_., 1977). Oxidation of ammonia (NH_3) in aqueous solution is not known to occur, but may not have been looked for adequately.

Chlorine Dioxide By-Products Found in Drinking Water and Selected Nonpotable Waters

The subcommittee found only one study of compounds that are generated in raw water as a result of treatment with chlorine dioxide. Stevens _et al_. (1978) reported several C_2 to C_8 aliphatic aldehydes, but no THM's as products of the treatment of Ohio River water with chlorine dioxide.

Chlorine Dioxide Reactions with Model Organic Compounds

There have been extensive investigations of reactions of chlorine dioxide with organic compounds, particularly phenols and amines. Results of these studies have been reviewed in detail in several articles and monographs (Gordon *et al.*, 1972; Masschelein, 1969; Miller, *et al*, 1978; Stevens *et al.*, 1978). Unfortunately, most of the studies were conducted in acidic solutions in which concentrations of chlorine dioxide and organic substrate were much greater than those encountered during water treatment. Consequently, the extent to which the findings are applicable to the pH values and concentrations of organic compounds that are found in drinking water sources is not clear. In addition, most reviewers did not specify the ranges of pH and concentrations to which their statements apply thereby making it difficult to separate the results of conclusions that pertain to highly dilute, nearly neutral aqueous solutions.

Since chlorine dioxide reduces to chlorite when it acts as a oxidant in the nearly neutral pH range, it functions as a one-electron aceptor. The immediate oxidation product must have an odd number of electrons to conform to the general definition of a free radical. Except for the studies of Lindgren with lignin simulators (Lindgren and Ericsson, 1969; Lindgren and Nilsson, 1972) and of Rosenblatt on reactions with tertiary amines (Rosenblatt, 1978l; Gordon et al., 1972), this aspect of the reaction of chlorine dioxide with organic materials has seldom been considered in defining reaction pathways and products. Yet, the reactivity of chlorine dioxide with organic material often differs greatly from that of other oxidants because of this one-electron transfer. Despite this, some investigators have stated that products resulting from treatment of organic material in natural waters with chlorine dioxide are generally similar to those found after ozonation (Buydens, 1970; Miller et al., 1978).

In a broad sense, chlorine dioxide is most reactive with tertiary amines and phenols (Masschelein, 1969; Rosenblatt, 1978), it is moderately reactive with olefins (Gordon et al., 1972), and its reactivity with alcohols and aldehydes, yielding the corresponding carboxylic acids, appears greater than that of ozone and aqueous chlorine (Masschelein, 1969; White et al., 1942). It is less reactive with secondary amines than with tertiary ones, and it is very unreactive toward primary amines (Gordon et al., 1972). As noted earlier, its reaction with ammonia is unknown (Miller et al., 1978). Chlorine dioxide is unreactive toward saturated aliphatic hydrocarbons and aliphatic side chains, but the latter may be split from aromatic rings or other functional groups. Saturated carboxylic acids, carbonyl compounds, and amino acids are usually inert with chlorine dioxide (Kennaugh, 1957, Sarkar, 1935).

Chlorine dioxide has sometimes been called a "pure" oxidant, which refers to its failure to form chlorinated derivatives. This is certainly incorrect, for numerous chlorinated aromatic compounds (Masschelein, 1969; Miller *et al.*, Paluch *et al.*, 1965) and some chlorinated aliphatic substances (Lindgren *et al.*, 1965) have been obtained from aqueous oxidations by chlorine dioxide. However, no THM's have been detected as reaction products of chlorine dioxide with organic materials, although investigators have looked for them carefully (Miller *et al.*, 1978; Vilagenes *et al*, 1977).

One complication is encountered when considering the reactions of chlorine dioxide with organic materials: the normal reaction product of chlorine dioxide, chlorite, may also be a reactive agent in some circumstances. A nucleophilic reagent (Rosenblatt, 1975), chlorite has been proposed as a possible source of some of the chlorinated products that are found after reaction of aromatic compounds with chlorine dioxide (Lindgren and Nilsson, 1972). Chlorite also reacts with aldehydes in neutral or mildly acidic aqueous solution yielding chlorine dioxide in accord with the following overall equation (White *et al.*, 1942):

$$RCHO + 3ClO_2^- + H^+ \longrightarrow RCO_2^- + 2ClO_2 + Cl^- + H_2O \qquad (21)$$

This reaction has been used, for example, in the colorimetric estimation of sugars (Jeanes and Isbell, 1941; Spinks and Porter, 1934). According to Lindgren and coworkers (Lindgren and Ericsson, 1969; Lindgren and

Nilsson, 1972). Reaction 21 may involve formation of hypochlorous acid as an initial product which then reacts on other chlorite to regenerate chlorine dioxide in a chain reaction or it reacts to chlorinate or oxidize other organic substrates. Formation of hypochlorous acid as a product in the oxidation of phenols by chlorine dioxide has also been postulated by Lindgren (Lindgren and Ericsson, 1969). His ideas are based on studies at pH 1 to 5 and millimolar or greater concentrations. The extent of these types of reactions for conditions of water treatment is not known.

Reactions of chlorine dioxide with phenol and substituted phenols have been studied by many investigators. An extensive list of references is given by Gordon *et al.* (1972). Probably the most detailed investigations that are applicable to conditions of water treatment have been those of Glabisz (1968) and Paluch (1964). See Gordon *et al.* (1972) for other citations. The major products of the reactions are quinones and chlorinated quinones, in which the initial ring structure is retained, and carboxylic acids such as oxalic ($\mathrm{HOOCCOOH}$), fumaric (trans-$\mathrm{HOOCCH{=}CHCOOH}$), and maleic acids (cis-$\mathrm{HOOCCH{=}CHCOOH}$), which result from rupture of the aromatic ring.

Phenol has been found to give 1,4-benzoquinone, 2-chloro-1,4-benzoquinone, 2,5-dichloro-1,4-benzoquinone, and the previously listed products of ring rupture (Masschelein, 1969). The chlorine-substituted products have been found to increase with decreasing ratio of chlorine dioxide to phenol, while ring rupture increases with increasing excess of chlorine dioxide over phenol.

Substituted phenols are also oxidized to p-quinones. Para substituents are often stripped away in the process, as is the case with p-nitrophenol, p-chlorophenol, and p-hydroxybenzaldehyde (Miller et al., 1978; Symmons et al., 1977). According to Glabisz (1968), p-alkylphenols and o- or m-dihydric phenols are more subject to ring cleavage than are other types of phenols.

There is some evidence that formation of chlorophenols precedes oxidation to chlorinated quinones (Glabisz, 1967). In his work with a limited concentration of chlorine dioxide that was mixed with 0.67 millimolar phenol, Spanggord found 2-chlorophenol, 4-chlorophenol, 2,6-dichlorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol, 2-chloro-2,4-dihydroxybenzene, resorcinol [C_6H_4-1,3-$(OH)_2$], and fumaric acid as products (Miller et al., 1978). Also, at the Water Supply Research Laboratory of the Environmental Protection Agency in Cincinnati, chlorophenols were observed as reaction products at a chlorine dioxide to phenol molar ratio of 0.8, but not at 3:1 or 14:1 (Miller et al., 1978). Interestingly, hydroquinone [C_6H_4-1,4-$(OH)_2$] was observed at all molar ratios. Some formation of polyquinones was also indicated.

Some other types of aromatic organic compounds are much less reactive than the phenols. For example, it has been reported that benzoic acid (C_6H_5COOH), benzenesulfonic acid

($C_6H_5SO_3H$) (Schmidt and Braunsdorf, 1922), and cinnamic acid ($C_6H_5CH{=}CHCOOH$) (Sarkar, 1935) do not react with chlorine dioxide. Benzylic acid [$(C_6H_5)_2C(OH)COOH$] reacts only slowly (Paluch et al., 1965). Dinitrophenols and trinitrophenols have also been found to be inert (Paluch, 1964). According to Gordon et al. (1972) anilines should react in much the same manner as do phenols. Reactions with amines have been studied extensively, particularly by Rosenblatt and coworkers (Gordon et al., 1972; Rosenblatt, 1978). Tertiary aliphatic amines are very reactive, undergoing a free-radical, oxidative dealkylation yielding aldehydes and secondary amines as products. The typical reaction with triethylamine [$(C_2H_5)_3N$] has the overall equation

$$(C_2H_5)_3N + 2ClO_2 + H_2O \rightarrow (C_2H_5)_2NH + CH_3CHO + 2H^+ + 2ClO_2^- \qquad (22)$$

Secondary amines react through a similar pathway, but more slowly. Most primary amines react only slightly (Rosenblatt, 1978). Benzylamines undergo a hydrogen-abstraction reaction and β-substituted amines may exhibit oxidative fragmentation as a result of α, β-scission.

Most amino acids are not reactive under conditions that prevail during water treatment (Kennaugh, 1957). In mildly acid solutions, tryptophan (2-amino-3-indolepropronic acid), is oxidized to indoxyl, isatin, and indigo red, the acetic acid side chain being concurrently removed (Fujii and Ukita, 1957; Schmidt and Braunsdorf, 1922). Tyrosine (p-

$HOC_6H_4CH_2CH(NH_2)COOH$) gives dopaquinone, and dopachrome at pH 4.5 (Hodgden and Ingols, 1954). Histidine (2-amino-4(5)-imidozole proprionic acid) is also somewhat reactive (Schmidt and Braunsdorf, 1922). At pH 3.5 cystine [$HOOCCH(NH_2)CH_2S-SCH_2CH(NH_2)COOH$] and methionine [$CH_3SCH_2CH_2CH(NH_2)COOH$] are oxidized at the sulfur atoms to bisulfoxide (=SO) and sulfonic acid (=SO_2H) and to sulfone (=SO_2), respectively, without reaction elsewhere in the molecules (Scherle, 1953).

Additional reactions of nitrogenous materials are described in considerable detail by Gordon _et al_. (1972). Most of the compounds that are covered are not known as common pollutants in water supplies. Consequently, their findings are not clearly relevant to water treatment with chlorine dioxide.

Studies with other materials have been sparse and have been confined mostly to acid conditions, pH 1 to 4, and to the concentrations between, 10^{-3} and 10^{-1}M, which are characteristic of pulp and paper bleaching. However, some of these studies have shown that a number of organic sturctures are quite unreactive with chlorine dioxide even under these conditions. Observed reactions are often attributed to hypochlorous acid or Cl_2 that are formed in other processes.

In contrast to ozone (O_3), chlorine dioxide is not highly reactive toward the olefinic double bond. The oleic chain of methyl oleate [$CH_3(CH_2)_7CH=CH(CH_2)_7COOCH_3$] (Leopold and Mutton, 1959; Lindgren and Svahn, 1966) or triolein (glyceryl trioleate) (Leopold and Mutton, 1959) reacts, even in acidic solution over several days, primarily by oxidation at a position α or β to the double bond or by scission at the α-β link. Cyclohexene (1,2,3,4-tetrahydrobenzene, C_6H_{10}) does undergo ring opening at the double bond, but also gives cyclohex-1-ene-3-one and 3-chlorocyclohexene as major initial products (Lindgren et al., 1965). With excess ClO_2, ring splitting occurs when dicarboxylic acids form. Moreover, Schmidt and Braunsdorf (1922) found fumaric, maleic, and crotonic ($CH_3CH{=}CHCOOH$) acids to be unreactive with chlorine dioxide.

Similarly, although primary alcohols may be oxidized to carboxylic acids or ketones in relatively concentrated acidic solutions, much less reactivity is apparent in dilute, nearly neutral aqueous media. For example, glucose at pH 2 oxidizes at the $-CH_2OH$ group, without opening of the furananose or pyranose ring (Flis et al., 1955) but Somsen (1960) found no reaction with ethanol or 2,3-butandiol [$CH_3CH(OH)CH(OH)CH_3$] at pH 7, even at 80°C.

Aldehyde groups are more reactive. For example, Somsen (1960) found that acetaldehyde (CH_3CHO), butyraldehyde ($CH_3CH_2CH_2CHO$), and acetoin [$CH_3CH(OH)COCH_3$] are oxidized to the corresponding carboxcylic acids at pH 7.0. Otto and Paluch (1965) reported that an aqueous dispersion of benzaldehyde (C_6H_5CHO) reacts violently with chlorine dioxide. On the other hand, Stevens et al. (1978) reported that several C_2 to C_8 aliphatic aldehydes were products of the treatment of Ohio River Water with chlorine dioxide.

The situation is complicated further by the reaction of chlorite ion with aldehydes to produce chlorine dioxide with concurrent oxidation of the aldehyde to carboxylic acid or carbon dioxide (Lindgren and Nilsson, 1972; White et al., 1942). Reaction takes place in neutral or slightly acidic solution:

$$H^+ + RCHO + 3ClO_2^- \dashrightarrow 2ClO_2 + RCO_2^- + Cl^- + H_2O \qquad (23)$$

Formaldehyde (HCHO), in particular, reacts very readily, but acetalydehyde, benzaldehyde, and reducing sugars are also known to react.

Hydrocarbons and simple carboxylic acids are generally inert towards dilute aqueous chlorine dioxide (Stevens et al., 1978). However, Reichert (1968a; 1968b) has shown that the polynuclear aromatic hydrocarbon, 3,4-benzpyrene ($C_{20}H_{12}$), reacts to give quinones and chlorinated derivatives. Reactions of polycyclic aromatic hydrocarbons have been described by Thielman (1972).

Humates and fulvates react with chlorine dioxide (Buydens, 1970; Fuchs and Leopold, 1927), as its use for the bleaching of colored waters attests, but the nature of the reactions is not known. Phenolic materials are reported to be released from the humic matrix under certain conditions (Buydens, 1970). Some investigators have conducted studies with model building units for lignin and humic acid; however, they have used acidic, high-concentration solutions. For example, vanillin [4-(HO)C_6H_3-3-(OCH_3)CHO] at pH 4 or less suffers ring rupture to give β-formylmuconic acid methyl ester (Sarkanen _et al._, 1962), while vanillyl alcohol [4-(HO)C_6H_3-3-(OCH_3)OH] at a final pH of 1 forms chlorinated benzoquinones (Dence _et al._, 1962). Under similar conditions veratryl alcohol [3,4-$(OCH_3)_2C_6H_3OH$] produces 4,5-dichloroveratrole [4,5-$Cl_2C_6H_4(OH_3)_2$] (Dence and Sarkanen, 1960). However, the pertinence of these findings to water treatment conditions is questionable, in view of the pH at which these reactions were observed.

Discussion

Much remains to be learned about the nature of the organic products that are formed in water supplies during oxidative treatment with chlorine dioxide. Clearly, chlorine dioxide, like other aqueous chemical oxidants, is selective in its attack on organic materials, so that only a small fraction, if any, is oxidized completely to carbon dioxide and water. The specific reactants and reaction products that are formed have been determined for only a few substances and, even then, in a very limited way.

Both oxygenated and chlorinated products may be formed, the latter being found most prominently in connection with the reactions of phenolic substances. Other products that might affect health are quinones and 1,2-epoxy compounds.

Formation of chlorinated products and quinones is greatest when the concentration of chlorine dioxide was limited in comparison with reactive organic matter. When the ratio of chlorine dioxide to organic carbon is large, e.g., 20:1 or more by weight, then many aromatic rings are broken and the principal products are carboxylic acids, ketones, and, possibly, aldehydes.

Unfortunately, economic considerations and concerns about possible toxicities of chlorine dioxide, chlorite, and chlorate will probably limit the use of chlorine dioxide in water treatment to concentrations that do not greatly exceed those of the organic carbon. Consequently, conditions that are conducive to the production of intermediate oxidation products are likely to be realized in practice. Therefore, the hygienic effects of these partial oxidation products--the quinones, chlorinated quinones, and epoxy compounds--need considering before any widespread usage of chlorine dioxide is undertaken.

On the other hand, chlorine dioxide is not known to produce THM's under any conditions (Love _et_ _al_., 1976; Mallevialle, 1976). It even seems not to be active in oxidizing bromide to bromine or hypobromite, with possible subsequent formation of brominated organic compounds (Vilagenes _et_ _al_., 1977). Its nonreactivity with ammonia is also an important and advantageous factor in the practical use of chlorine dioxide.

Research Recommendations

Primary targets for research are the potential toxicities and carcinogenicities of chlorine dioxide, chlorite, and chlorate.

Secondly, there is a need for much greater knowledge of the organic products that are formed during the treatment of humates and fulvates with chlorine dioxide and of the hygienic properties of those products, both individually and collectively.

Finally, additional research is needed on the reaction pathways and products for the interaction of specific aquatic pollutants with chlorine dioxide under conditions approximating those anticipated during the preparation of drinking water.

OZONE

Although ozone (O_3) has been used as a disinfectant of water for over eight decades (Lawrence and Cappelli, 1977), relatively little is known about its chemistry as an oxidizing agent of organic and inorganic solutes in aqueous solution. On the other hand, ozone reactions in nonaqueous systems have been studied thoroughly, mainly because of the widespread use of ozone as a degradative tool in the elucidation of organic structure (Murray, 1968). While it is probably true that much of this knowledge may be transferred to aqueous systems, particularly at low pH values (Hoigne and Bader, 1975), few definitive mechanistic studies have been conducted to confirm this view. Thus, a discussion of the chemistry of ozone by-products that are formed during water treatment is severely limited by a lack of specifically designed studies, and by the poor definition of the organic materials involved.

This unfortunate situation probably will not prevail very long. Several studies in progress have been stimulated by the prospect that ozone will be used increasingly as a water treatment chemical and by the need for more information on by-products that may be formed from ozone oxidations of water contaminants. Some of these studies have been reported in preliminary form at scientific meetings (Rice and Cotruvo, 1978). Combined with the earlier literature, they allow one to see an emerging picture of ozone by-product chemistry. Clearly, much is left to be accomplished in this area.

This part of the report is divided into four sections. In the first, some of the physical and chemical properties of ozone as they pertain to its use as a water disinfectant are examined. The second lists those few cases where reaction by-products from actual in-plant use of ozone have been isolated and identified. The third section examines some studies that have been conducted with model compounds. The final section discusses reactions that are thought to be possible on the basis of the known chemistry of ozone and the various substrates that occur in municipal drinking waters.

Properties of Ozone

Ozone is a gas at normal ambient temperatures. It is unstable and highly reactive (Manley and Niegowski, 1967). Ozone is one of the most powerful chemical ozidizing agents known, having a standard redox potential in water of 2.07 volts at 25°C. (For comparison, the value for hypochlorous acid (HOCl) is 1.49 volts). As a result, ozone is capable of oxidizing organic and inorganic compounds--in most cases with great faciltity. It is also particularly adept at oxidizing carbon-carbon double bonds, other multiple bonds, aromatic compounds, and most nitrogenous and sulfurous compounds in which the element is at a low oxidation state.

Ozone is moderately soluble in water. Manley and Niegowski (1967) have reported solubility data at various temperatures; however, saturated solutions of ozone in water seldom occur due to the decomposition of ozone or its tendency to react with dissolved materials in water. In practice, ozone doses of a few milligrams per liter are most commonly used in water treatment applications.

Ozone gas is generated at the site of application because concentrated mixtures of the substance are subject to detonation. Various reports place an upper limit of 9% to 20% ozone, but in practice, ozone generators usually produce 1% to 2% ozone when air is used and 3% to 5% when pure oxygen is used as the carrier (Klein et al., 1975).

Ozone is generated by electrical discharge in the air or oxygen stream (Klein et al., 1975), by photochemical processes involving ultraviolet radiation (Briner, 1959) or by other methods. It decomposes in aqueous solution by a complex mechanism yielding oxygen and a small amount of hydrogen peroxide (H_2O_2) (Kilpatrick et al., 1956; Stumm, 1954). Decomposition is catalyzed by hydroxide (OH^-). Therefore, it occurs more rapidly at high pH values. Most importantly, the decomposition occurs at such a fast rate in neutral to basic solutions that an active disinfectant residual cannot be maintained in a water supply distribution that uses ozone as the primary disinfectant (Falk and Moyer, 1978; Symons, 1977).

Hoigne and Bader have shown that aqueous ozone chemistry is explicable in terms of two mechanisms: one involves "direct" reactions of ozone; the other involves reactions of active hydroxyl radical intermediates (Hoigne and Bader, 1975, 1976, 1977, 1978a, 1978b). Hoigne has pointed out that the reaction involving radical intermediates is accelerated at high pH values and may yield a variety of products, some of which may serve as radical chain carriers or as chain terminating agents. The nature of the medium may have a profound effect on the rate of the radical reaction, particularly if it contains amines, carbonates, and organic carbon (Hoigne, 1978a).

The direct reaction of ozone with organic substrates has been the subject of numerous studies, but in most cases the solvent has not been water (Bailey, 1975). The reaction with olefin compounds has been the most studied. It is now agreed that the so-called Criegee mechanism (Criegee, 1959) explains most of the products formed. In general, aqueous ozonolysis reactions of olefins would be expected to yield ketones and carboxylic acids plus small amounts of hydroxyhydroperoxides (Bailey, 1975).

Aromatic compounds, amines, acetylenes, and many other compounds have been subjected to ozonolysis in aqueous solution. The results of these studies have been reviewed by Bailey (1975), Oehlschlaeger (1978), Maggiolo (1978), and Rice (1977). These studies are summarized below. However, few studies have been conducted over the full range of conditions that are likely to prevail in a typical water treatment plant. The strong influence of pH and interfering substances such as ammonia (NH_3) and carbonate (CO_3^{--}) on ozone reactions may seriously limit the effectiveness of such studies. Nonetheless, a review of the available information confirms the need for further research to determine ozone by-products.

Ozone By-Products Found in Drinking Water or Selected Nonpotable Waters

Ozone is now used in over 1,000 drinking water plants in Europe, and is being incorporated into some new plants in North America predominantly in the Province of Quebec (Miller and Rice, 1978). In view of this experience, it is remarkable that so little is known about the formation of the by-products from organic or inorganic materials in the influent water. The subcommittee surveyed leading authorities in the European water treatment industry. With the exceptions noted below, they expressed no knowledge of "before and after" ozonization studies to determine what, if any, by-products of the ozonization process may be present in treated water. Similarly, the U.S. Environmental Protection Agency (EPA) authorities in this field, as well as private and academic scientist, purport to know of no such studies with the exception of a few that are in progress.

In the waterworks in Zurich, Switzerland, investigators have studied the by-products of ozonization (Schalekamp, 1978). These studies, which where conducted with assistance from the Swiss Federal Institute for Water Resources and Water Pollution Control (EAWAG), demonstrated that a series of aldehydes [n-hexanal ($C_5H_{11}CHO$), n-heptanal ($C_6H_{13}CHO$), n-octanal ($C_7H_{15}CHO$), and n-nonanal ($C_8H_{17}CHO$)] that were present after ozonization had not been present beforehand.

The origin of these aldehydes is not fully understood, however, Sievers and coworkers (1977a), while studying onzonized secondary wastewater effluent from a treatment facility in Estes Park, Colorado, found the same compounds. They also found n-pentanal (C_4H_9CHO) and the hydrocarbons n-hexane (C_6H_{14}), n-heptane (C_7H_{16}), n-octane (C_8H_{18}), and n-nonane (C_9H_{20}). Moreover, the concentration of toluene ($C_6H_5CH_3$) apparently increased.

Removal of organics at the water treatment plant in Rouen-la-Chapelle, France has been discussed by Rice et al. (1978). Although they did not describe the details of the analytical procedures, their data show that ozonization produces no increases in the concentrations of the several organic materials that were monitored.

Other than these three studies, little is known about the reaction products from ozonization of natural or treated waters. Chian and Kuo (1976) and Kinman et al. (1978) have reported on the ozonization of secondary treated wastewater, but they found no new compounds resulting from the ozonolysis process. Glaze and coworkers and scientists at the Research Institute of the Illinois Institute of Technology (Klein, 1978, private communication) are involved in studies that are directed to this goal, but their results are not yet available.

The apparent lack of data on this subject may be attributed to the preoccupation of trace analytical chemists with the methods of gas chromatography (GC) and combined GC-mass spectrometry (GC/MS) for the analysis of organic materials at the parts per million level and below. These methods have proven to be invaluable for the analysis of volatile compounds, particularly nonpolar compounds which may be preconcentrated by various partitioning techniques; however, they have not been perfected for the analysis of very polar compounds, which may result from oxidation processes. Nor are these methods useful for labile compounds such as peroxidic compounds, ozonization intermediates that may affect health. Thus, it appears that investigators have yet to demonstrate the important products that are produced from the ozonization of organic materials in untreated and treated waters. To do so, these investigators will presumably use techniques such as liquid chromatography, fourier transform infrared spectroscopy, etc.

Ozonization of Model Organic and Inorganic Compounds

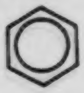
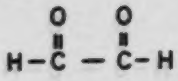
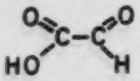
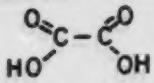
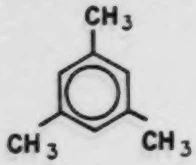
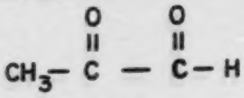
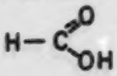
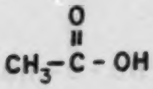
Rice (1977) has reviewed several studies on the reaction products from the ozonization of various organic and inorganic compounds in aqueous solution. A recent monograph by Rice and Cotruvo (1978) contains papers from a 1976 conference on the products arising from organic materials treated with ozone or chlorine dioxide (ClO_2). Together these two references contain the vast majority of papers on this subject. No critical examinations of the reliability of the data contained in the papers have been attempted in this report.

Tables 11 through 18 list products of ozonization of various classes of organic compounds. In most of the studies listed, if ozone was measured at all, it was simply reported that ozone was bubbled, at a measured gas phase level, into water plus substrate. Exhausting ozone gas or decomposition by virtue of contact with the bubbler first, etc. were generally not measured. Similarly, pH was seldom measured, despite its importance in such studies.

Reactions with Inorganic Compounds

In general, ozone oxidizes inorganic elements to a stable high oxidation state. Among the common metallic elements, iron is converted to the ferric state (Mallevialle *et al.*, 1978) and manganese to either the IV or VII oxidation state, manganate (MnO_4^{--}) or manganese dioxide

TABLE 11 Summary of Ozonation Byproducts of Organic Compounds
Aromatic Compounds: Benzene and Its Homologs

Substrate	Products	Reference
Benzene 	Glyoxal  $\mathrm{H-\overset{O}{\overset{\parallel}{C}}-\overset{O}{\overset{\parallel}{C}}-H}$	Jurs, 1966 in Rice, 1977
	Glyoxylic acid 	
	Oxalic acid 	
1,3,5,-Trimethylbenzene 	Methylglyoxal[a]  $\mathrm{CH_3-\overset{O}{\overset{\parallel}{C}}-\overset{O}{\overset{\parallel}{C}}-H}$	Cerkinsky and Trahtman, 1972
	Formic acid 	
	Acetic acid  $\mathrm{CH_3-\overset{O}{\overset{\parallel}{C}}-OH}$	

[a] Principal product.

TABLE 12 Summary of Ozonation Byproducts of Organic Compounds
Aromatic Compounds: Polynuclear Aromatics

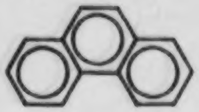
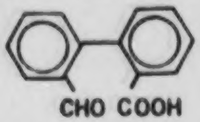
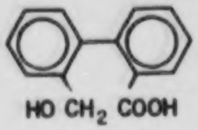
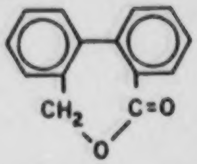
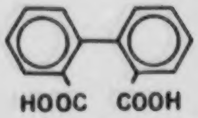
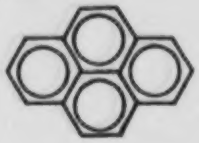
Substrate	Products	Reference
Phenanthrene (in aqueous methanol) 	2′-Formyl-2-biphenylcarboxylic acid  2′-Hydroxymethyl-2-biphenylcarboxylic acid  Diphenide  Diphenic acid 	Sturrock *et al.*, 1963
Pyrene 	Acetic acid CH_3COOH Oxalic acid HOOCCOOH Plus other water soluble acids.	Kinney and Friedman, 1952

TABLE 12 (continued)

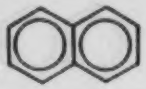
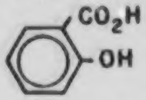
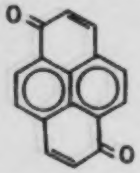
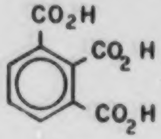
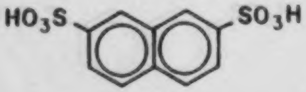
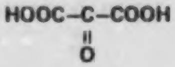
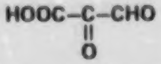
Naphthalene 	Salicylic acid 	Jurs, 1966
3,8-Pyrenequinone 	1,2,3,4,-Benzenetetracarboxylic acid 	Ahmed and Kinney, 1950
Naphthalene-2,7-disulfonic acid 	Formic acid HCOOH Oxalic acid HOOCCOOH Sulfate SO_4^{2-} Glyoxal OHCCHO Mesoxalic acid  $HOOC{-}\underset{\overset{\Vert}{O}}{C}{-}COOH$ Mesoxalic acid semialdehyde  $HOOC{-}\underset{\overset{\Vert}{O}}{C}{-}CHO$	Gilbert, 1976b

TABLE 13 Summary of Ozonation Byproducts or Organic Compounds
Aromatic Compounds: Phenolics

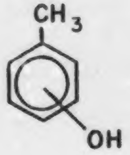
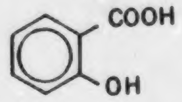
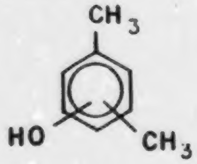
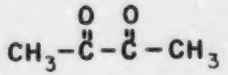
Substrate	Products	Reference
Cresols 	Salicylic acid[a] (from o-Cresol)  Maleic acid HOOCCH=CHCOOH (cis) Acetic acid CH_3COOH Oxalic acid HOOCCOOH Glyoxylic acid HOOCCHO Mesotartaric acid HOOC–CH(OH)–CH(OH)–COOH Glycolic acid $HOCH_2$–COOH	Bauch *et al.*, 1970
Xylenols 	Same Products as from Cresols plus Biacetyl  $CH_3-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-CH_3$	Bauch *et al.*, 1970

TABLE 13 (continued)

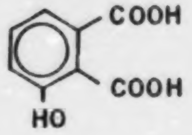
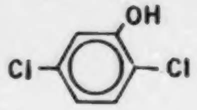
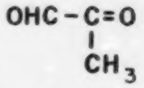
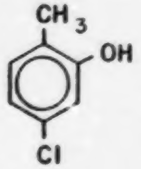
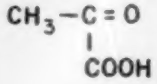
	Hydroxyphthalic acid 	
2,4-Dichlorophenol 	Formic acid $HCOOH$ Oxalic acid $HOOCCOOH$ Chloride ion Cl^-	Gilbert, 1976a
	Chloride ion[a] Cl^- Acetic acid[b] CH_3COOH Formic acid $HCOOH$ Methyglyoxal[a]  $OHC-\underset{CH_3}{C}=O$	Gilbert, 1976b
4-Chloro-o-Cresol 	Pyruvic acid[b]  $CH_3-\underset{COOH}{C}=O$	Gilbert, 1976b

TABLE 13 (continued)

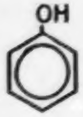
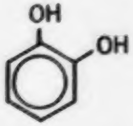
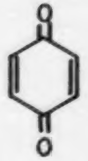
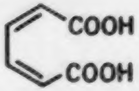
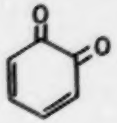
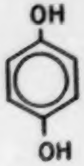
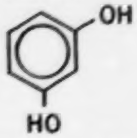
Substrate	Products	Reference
Phenol 	Catechol[a]  P-Quinone  Muconic acid  Fumaric acid HOOC–CH=CH–COOH (trans) Oxalic acid HOOC–COOH	Eisenhauer, 1968
Phenol	Maleic acid HOOC–CH=CH–COOH (cis) Tartaric acid HOOC–CHOH–CHOH–COOH Glyoxylic acid HOOC–CHO Oxalic acid HOOC–COOH	Bauch and Burchard, 1970

TABLE 13 (continued)

Phenol	P-Quinone, Catechol (as above) O-Quinone 	Hydroquinone 	Mallevialle, 1975
Phenol	Catechol (as above) Resorcinol 		Spanggord and McClurg, 1976
Phenol	Glyoxylic acid, Hydroquinone,[a] Catechol, Oxalic acid (as above) Glyoxal[b] OHC–CHO		Gould and Weber, 1976

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[a] Initial product.

[b] Intermediate product.

TABLE 14 Summary of Ozonation Byproducts of Organic Compounds
Aromatic Compounds: Miscellaneous

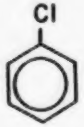
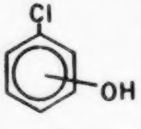
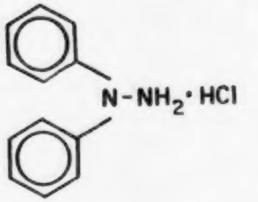
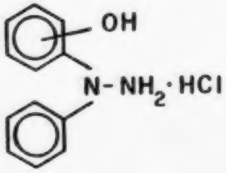
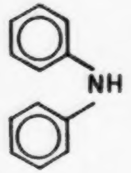
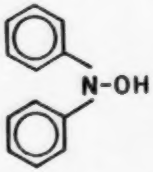
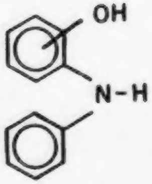
Substrate	Products	Reference
Chlorobenzene 	o-, m-, and p-Chlorophenols  Chlorotartaric acid $HOOC{-}CH(OH){-}CH(Cl){-}COOH$ Plus other ring ruptures products as from chlorophenols	Bauch *et al.*, 1970
Unsym-Diphenylhydrazine hydrochloride 	1-Hydroxypenyl-1-phenyl hydrazirfe hydrochloride  Diphenylamine  Diphenyl-N-hydroxyl amine  Hydroxyphenyl-phenylamine 	Spanggord and McClurg, 1976

TABLE 14 (continued)

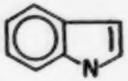
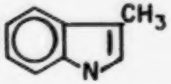
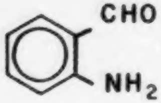
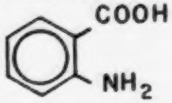
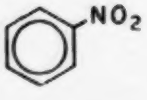
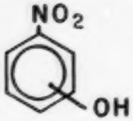
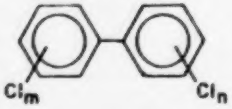
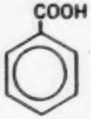
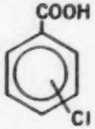
Indole  Skatole 	2-Amino-benzaldehyde  2-Amino-benzoic acid 	Jurs, 1966
Nitrobenzene 	o-, m-, and p-Nitrophenols 	Westgate Research Corp., 1978
PCB Mixture 	Benzoic acid  Chloro-benzoic acids  Chloride ion Cl^- Hydrogen perioxide H_2O_2	Yokoyama *et al.*, 1974

TABLE 14 (continued)

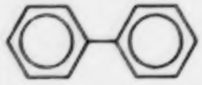
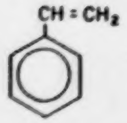
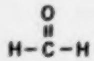
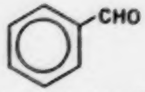
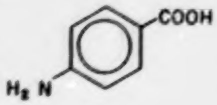
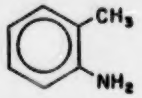
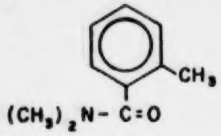
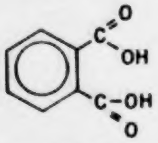
Substrate	Products	Reference
Biphenyl 	Glyoxal OHCCHO Glyoxylic acid HOOCCHO Oxalic acid HOOCCOOH	Yokoyama *et al.*, 1974
Styrene 	 $H-\overset{O}{\overset{\|}{C}}-H$  Formaldehyde; benzaldehyde[a] Benzoic acid	Yocum, 1976
4-Aminobenzoic acid 	Ammonia NH_3 Nitrate NO_3^- Formic acid HCOOH Oxalic acid (as above)	Gilbert, 1976b

TABLE 14 (continued)

o-Toluidine 	Acetic and oxalic acids (as above)	Chian and Kuo, 1976
N,N-Dimethyl-m-toluamide 	Formic, acetic, and oxalic acids (as above)	Chian and Kuo, 1976
Phthalic acid 	Oxalic and acetic acids (as above)	Kinney and Freidman, 1952

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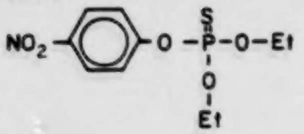
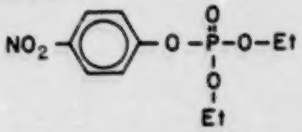
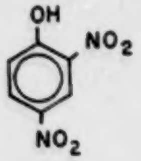
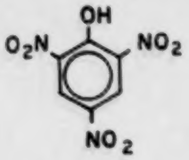
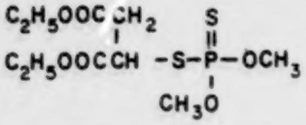
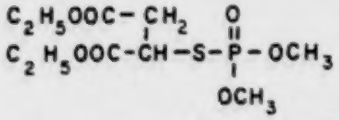
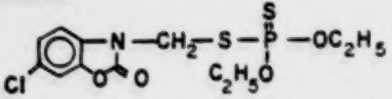
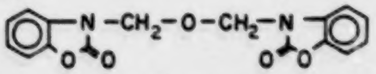
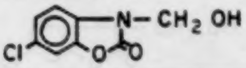
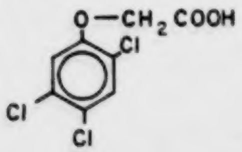
[a] Initial product.

TABLE 15 Summary of Ozonation Byproducts of Organic Compounds Humic Acids and Similar Natural Products

Substrate	Products	Reference
Humic acid (Aldrich Chemical)	Malonic acid[a] $HOOC-CH_2-COOH$	Lawrence, 1977
	Hexanoic acid[a] $CH_3(CH_2)_4COOH$	
	Succinic acid[a,b] $HOOC-(CH_2)_2-COOH$	
	Heptanoic acid $CH_3(CH_2)_5COOH$	
	Benzoic acid[a,b] C_6H_5-COOH	
	Octanoic acid $CH_3-(CH_2)_6-COOH$	
	Glutaric acid[a,b] $HOOC-(CH_2)_3-COOH$	
	Adipic acid[a,b] $HOOC-(CH_2)_4-COOH$	
	Pimelic acid[a,b] $HOOC-(CH_2)_5-COOH$	
	Suberic acid[a,b] $HOOC-(CH_2)_6-COOH$	
	Azelaic acid[a,b] $HOOC-(CH_2)_7-COOH$	
	Sebacic acid[a,b] $HOOC-(CH_2)_8-COOH$	
	1,2,3,-Propane tricarboxylic acid[a,b] $HOOCCH_2CH(COOH)CH_2COOH$	
	Di-, tri-, tetra-, and penta-carboxylic Benzenes	
	1,2,3,4-Butane tetracarboxylic acid	
Humic acid (Peat)	Crenic and Apocrenic acids	Shevchenko and Taran, 1966
	Oxalic acid $HOOCCOOH$	
Humic acid (Coal Derived)	Oxalic acid (as above) plus "ozone-resistant acids"	Ahmed and Kinney, 1950

[a] Also identified from ozonized lignosulfonic acids.
[b] Also identified from ozonized tannic acid.

TABLE 16 Summary of Ozonation Byproducts of Organic Compounds
Pesticides

Substrate	Products	Reference
Parathion 	Paraoxon 	Gunther *et al.*, 1970
	Paraoxon[a] (as above) 2,4-Dinitrophenol  Picric acid (2,4,6-Trinitrophenol)  Sulfuric acid H_2SO_4 Phosphoric acid H_3PO_4	Richard and Brener, 1976
Malathion  $\begin{array}{l} C_2H_5OOC\,CH_2 \\ C_2H_5OOCCH-S-\underset{CH_3O}{\overset{S}{\overset{\Vert}{P}}}-OCH_3 \end{array}$	Malaoxon  $\begin{array}{l} C_2H_5OOC-CH_2 \\ C_2H_5OOC-CH-S-\underset{OCH_3}{\overset{O}{\overset{\Vert}{P}}}-OCH_3 \end{array}$	Richard and Brener, 1976
Phosalone 	Bis(chloro-6-oxo-2-benzoxazolyl-3-methyl) ether.  Hydroxymethyl-3-chlorobenzoxazolone 	Richard and Brener, 1976
2,4,5-Trichlorophenoxyacetic acid 	Dichloromaleic acid[a] HOOC–CHCl–CHCl–COOH Glycolic acid HCH_2COOH Oxalic acid HOOCCOOH Chloride Cl^-	Weil *et al.*, 1977

[a] Initial product.

TABLE 17 Summary of Ozonation Byproducts of Organic Compounds
Aliphatic Compounds

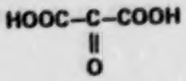
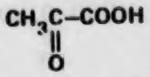
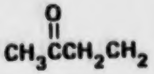
Substrate	Products	Reference
2-Hydroxylpropane $CH_3CH(OH)CH_3$	Mesoxalic acid  $HOOC{-}\underset{\overset{\|}{O}}{C}{-}COOH$ Acetone[a] CH_3COCH_3 Oxalic acid $HOOCCOOH$ Pyruvic acid  $CH_3\underset{\overset{\|}{O}}{C}{-}COOH$	Kuo *et al.*, 1977
Acetic acid CH_3COOH	Glyoxylic acid $CHO{-}COOH$ Oxalic acid (as above)	Kuo *et al.*, 1977
Propanol $CH_2CH_2CH_2OH$	Propanal CH_3CH_2CHO	Chian and Kuo, 1976
Propanoic acid CH_3CH_2COOH	Acetone (as above)	Chian and Kuo, 1976
Methylethyl ketone  $CH_3\overset{\overset{O}{\|}}{C}CH_2CH_2$	Acetate ion CH_3COO^-	Chian and Kuo, 1976

TABLE 17 (continued)

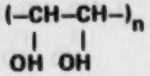
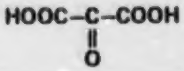
Diethylether $CH_3CH_2OCH_2CH_3$	Ethyl acetate $CH_3CH_2OOCCH_3$ Acetate ion (as above) Acetaldehyde CH_3CHO Methyl Formate $HCOOCH_3$ Ethanol C_2H_5OH Acetone[b], ethyl formate[b]	Chian and Kuo, 1976
Polyethylene glycol  $(-\underset{OH}{CH}-\underset{OH}{CH}-)_n$	Ethylene glycol; diethylene glycol; triethylene glycol; pentaethylene glycol; organic acids; aldehydes	Yokoyama *et al.*, 1974
Malonic acid $HOOC-CH_2-COOH$	Hydroxymalonic acid $HOOC-CH(OH)-COOH$ Ketomalonic acid  $HOOC-\underset{\underset{O}{\|}}{C}-COOH$	Dobinson, 1960
Maleic acid (cis) $HOOC-CH{=}CH-COOH$	Glyoxylic acid[c] (as above) Formic acid[c] $HCOOH$ Glvoxal $OHCCHO$	Gilbert, 1976a

TABLE 17 (continued)

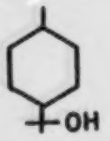
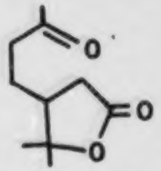
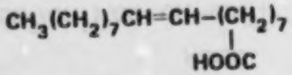
Substrate	Products	Reference
α-Terpineol 	4-(3-Oxobutanyl)-5,5-dimethyl-2-furanone 	Carlson and Caple, 1977
Oleic acid  $CH_3(CH_2)_7CH{=}CH{-}(CH_2)_7{-}COOH$	n-Nonyl aldehyde $CH_3(CH_2)_7CHO$	Carlson and Caple, 1977
	Octanoic acid[d] $CH_3(CH_2)_6COOH$	
	Suberic acid $HOOC{-}(CH_2)_6{-}COOH$	
	Azelaic acid[d] $HOOC{-}(CH_2)_7{-}COOH$	
	Azeladehydic acid[d] $OHC{-}(CH_2)_7{-}COOH$	
	9,10-Dihydroxysteric acid $CH_3(CH_2)_7{-}CHOH{-}CHOH{-}(CH_2)_7{-}COOH$	
	9,10-Oxyoleic acid $CH_3(CH_2)_7CH(O)CH(CH_2)_7COOH$	

TABLE 17 (continued)

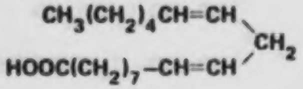
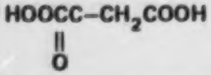
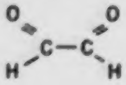
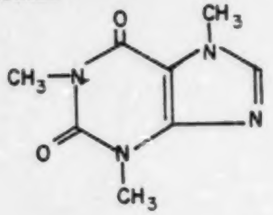
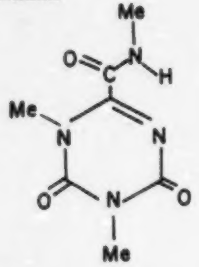
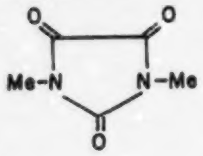
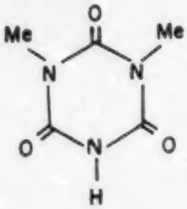
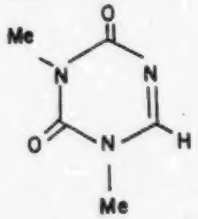
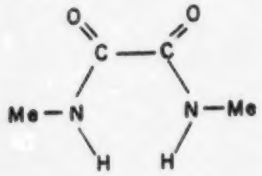
Linoleic acid  $CH_3(CH_2)_4CH{=}CH{-}CH_2{-}CH{=}CH{-}(CH_2)_7COOH$	n-Hexanal $CH_3(CH_2)_4CHO$ n-Hexanoic acid $CH_3(CH_2)_4COOH$ Azelaldehydic acid $OHC{-}(CH_2)_7{-}COOH$ Azelaic acid $HOOC{-}(CH_2)_7{-}COOH$ 3-Nonenal $CH_3(CH_2)_4CH{=}CH{-}CH_2CHO$	Carlson and Caple, 1977
Oxalacetic acid  $HOOC\underset{\underset{O}{\Vert}}{C}{-}CH_2COOH$	Mesoxalic acid (as above) Oxalic and Glyoxylic acids (as above)	Gilbert, 1976b
Dihydroxyfumaric acid $HOOC{-}C(OH){=}(OH)COOH$	Oxalic acid^{c} (as above) Dihydroxytartaric $HOOC{-}C(OH)_2{-}COOH$ Mesoxalic acid (as above) Mesoxalic acid Semialdehyde $HOOCCOCHO$	Gilbert, 1976b
Glyoxal 	Oxalic acid (as above)	Gilbert, 1976b

TABLE 17 (continued)

Substrate	Products	Reference
Tartronic acid $HOOCCH(OH)-COOH$	Mesoxalic acid (as above)	Gilbert, 1976b
Malonic acid $HOOCCH_2COOH$	Oxalic acid (as above) Mesoxalic acid (as above) Tartronic acid[e] $HOOCCH(OH)COOH$	Gilbert, 1976b
Diethylamine $(C_2H_5)_2NH$	Acetaldoxime $CH_3CH{=}NOH$	Spanggord and McClurg, 1976

[a] Initial product.
[b] Minor product.
[c] Major product.
[d] Also identified by Spanggord and McClurg, 1976.
[e] Intermediate product.

TABLE 18 Summary of Ozonation Byproducts of Organic Compounds
Miscellaneous Compounds

Substrate	Products		Reference
Caffeine 	1,3-Dimethyl-2,6-dioxo-4-methylcarbamyl-S-triazine 	Dimethylparabanic acid 	Sievers *et al.*, 1977a
	3,5-Dimethyl-2,4,6-trioxo-S-triazine 	1,3-Dimethyl-2,4-dioxo-S-triazine 	
	N,N′-Dimethyl-oxamide 		

(MnO_2), and permanganate (MnO_4^-), respectively. Ozone followed by filtration has been used to reduce iron and manganese to levels below those required by public health standards (Kjos *et al.*, 1975). Ozone effectively removes a variety of trace metals as insoluble oxides at pH values from 7 to 9 (Netzer and Bowers, 1975). Sulfur in organic compounds often is converted to sulfate (SO_4^{--}) (Gunther *et al.*; Mallevialle *et al.*, 1978), although in this and other cases the lower oxidation states of the element will result if small amounts of ozone are used.

Bromine is oxidized first to hypobromite (OBr^-) and then to bromate (BrO_3^-) (Ingols, 1978). Although hypobromite may be unstable in comparison to bromate under usual conditions, its transient existence is indicated by the formation of bromoform ($CHBr_3$) from the ozonization of seawater (Helz *et al.*, 1978). Presumably one would also find iodinated organics under the same conditions.

The ammonium ion (NH_4^+) is resistant to ozone attack, but above pH 7 ammonia is oxidized to nitrate (NO_3^-), presumably with several forms of intermediaries including nitrite (NO_2^-) (Hoigne and Bader, 1978b; Huibers *et al.*, 1969; Singer and Zilli, 1975; Wynn *et al.*, 1973). Organic amines have yielded both nitrate and nitrite (Rogozhkin *et al.*, 1970). Again, the dose of ozone could determine the relative yield of the oxidized forms in many cases.

Ozone has been used extensively for the oxidation of free and complexed cyanide (CN^-) to cyanate (OCN^-) (Bollyky, 1975; Garrison et al., 1975; Mathieu, 1975; Selm, 1959).

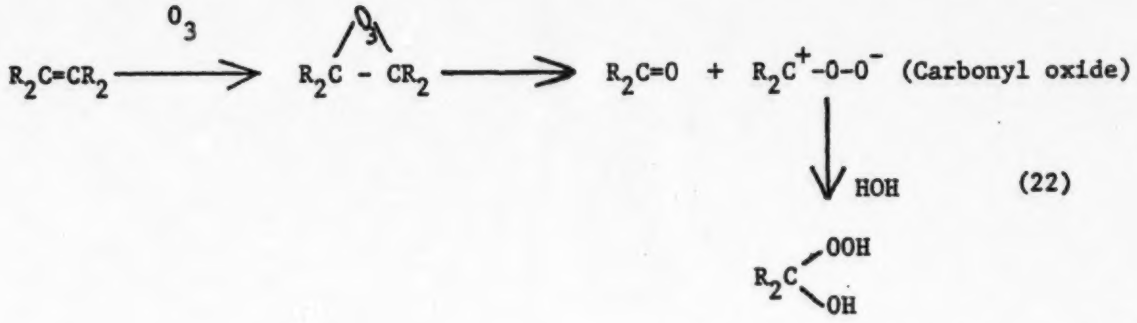
Inferences of Possible Ozone Reaction By-Products

As indicated above, attempts to identify new by-products from the reaction of ozone with organic materials in water have been limited to rather conventional separation and identification methods. As expected, rather conventional compounds have been identified as reaction by-products; however, some of them have important characteristics. For example, paroxon ($C_9H_{10}O_2$) from parathion ($C_{10}H_{14}NO_5PS$) is reported to be more toxic than its precusor. Nonetheless, the most important by-products from many organic substrates may have been overlooked because of shortcomings of the analytical method that was used. There is indirect evidence of the presence of these species. Carlson and Caple (1977) observed residual oxidizing species in ozonized water long after ozone would have decomposed. Moreover, analysis of ozone in water by a purge method yields only 81% of the value that was obtained by the direct iodide/thiosulfate titration procedure (Brody, 1975).

It appears that studies have not shown that many of the labile intermediates, such as hydroxyhydroperoxides, peroxides, etc., are absent in ozonized organic solutions. Investigators simply have not looked for them carefully.

These by-products may be of considerable significance to human health and need evaluating in this respect.

The Criegee mechanism for the reaction of ozone with carbon-carbon double bonds (Reaction 23) predicts that a hydroxyhydroperoxide will be formed as an intermediate when water is used as the solvent (Criegee, 1959).



(22)

hydroxy hydroperoxide

Moreover, it has been reported (Oehlschaeger, 1978) that various polymeric peroxides form in nonaqueous solvents, but there have been no known studies to determine if this occurs in water.

Epoxide Formation

The possibility that ozone will produce potentially dangerous epoxides has been the subject of much informal speculation, but few studies on the subject have been reported. Carlson and Caple (1977) found oleic acid oxide from the aqueous phase ozonization of oleic acid, but subsequent experiments indicated that the compound results from the oxidation of the acid by peracid intermediates in the reaction mixture arising from the autooxidation of aldehydic products. No examples of epoxide formation from polynuclear aromatic compounds with aqueous ozone have been found, but the posibility that these compounds exist as minor products can not be dismissed. Further study in this area is needed.

CONCLUSIONS

The preceding sections of this report summarize the results of an extensive survey of the chemistry of disinfectants that are or may be used in water treatment. Although it has been recognized since 1974 that chlorine produces potentially harmful by-products, such as the ubiquitous chloroform, little attention has been given to the other prospective disinfectants and oxidants such as ozone, chlorine dioxide, chloramines, and the other halogens, bromine and iodine. Quite apart from the question of the efficacy of these substances as alternative disinfectants, there remains the question, "Will the substitution of a disinfectant for chlorine in water treatment merely produce a different set of by-products whose effects on human health may be as significant, or more so, than those by-products known to be produced from chlorine?"

Unfortunately, a definitive answer cannot yet be given to this question. The surveys that are reported in the foregoing sections illustrate the lack of information on this subject even for the two common disinfectant chemicals, chlorine and ozone. There have been few studies in which the water of a treatment plant has been characterized before and after treatment, and, in most of these cases, chlorine was used as the disinfectant chemical. There are only two studies of water, which had had ozone treatment, which is common in Western Europe, and no in-plant studies of water for which chlorine dioxide or the other halogens were used.

The authors were forced to resort to a survey of laboratory studies in which the various disinfectants were used or to works where a secondary wastewater was treated with one of the alternative disinfectants. As expected, these surveys showed that each disinfectant produces a set of by-product compounds that reflect the nature of the starting materials and the disinfectants that were used. Unfortunately, many of the laboratory studies were conducted under conditions that were not comparable to those in water treatment. For example, the initial concentrations of starting materials or disinfectant doses were too high, pH was too low, etc. Moreover, in most cases, the characterization of the by-products was incomplete or in the other ways equivocated, so that a direct parallel could not be drawn between the laboratory results and those which could be expected in an actual water treatment plant.

Nonetheless, it is clear that each disinfectant chemical that was examined in this survey produces by-products that may occur in actual water treatment applications. Of particular concern are the following substances that result from the use of the various disinfectants.

- From chlorine: the trihalomethanes (THM's), trichloroacetone (CCl_3COCH_3), and other largely uncharacterized chlorinated and oxidized intermediates that are formed from the complex set of precursors in natural waters; chloramines; chlorophenols; and the largely unknown products of dechlorination.

- From ozone: epoxides which may in principle result from unsaturated substrates such as oleic acid, although none have yet been found in drinking water; peroxides and other highly oxidized intermediates such as glyoxal (OHCCHO) and methylglyoxal (CH_3COCHO) from aromatic precursors.
- From bromine and iodine: THM's and other bromine and iodine analogs of chlorinated species; bromophenols, bromoindoles, and bromoanisoles; plus the halogens themselves, which may remain in drinking water as residual.
- From chlorine dioxide: chlorinated aromatic compounds; chlorate (ClO_3^-) and chlorite (ClO_2^-) which are often present as by-product or unreacted starting material from production of chloride dioxide; and chlorine dioxide itself.

This list, incomplete as it is, is compelling in that it shows that each disinfectant produces chemical side effects that should be examined in more detail before the disinfectant is widely adopted for water treatment. It is clear that each of these disinfectants, being highly reactive chemical agents, will have inevitable side effects. Even in the case of chlorine, all of these side effects are not fully understood. This situation is due partly to the lack of systematic studies designed to evaluate by-products from each alternative disinfectant under actual water treatment conditions. But of equal importance is the need for these studies to utilize the complete spectrum of analytical instrumentation for the detection and identification of by-product compounds, not just for compounds that are amenable to extraction and GC/MS analysis. It appears that a preoccupation with these techniques has led chemists to omit from their characterizations those very polar, water-soluble components that might elude extraction and those high molecular weight or labile compounds which might not be detectable by GC/MS.

The subcommittee hopes that this report will stimulate future research that will avoid these deficiencies and provide more complete information on the by-products that are associated with the use of each alternative disinfectant under realistic conditions.

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